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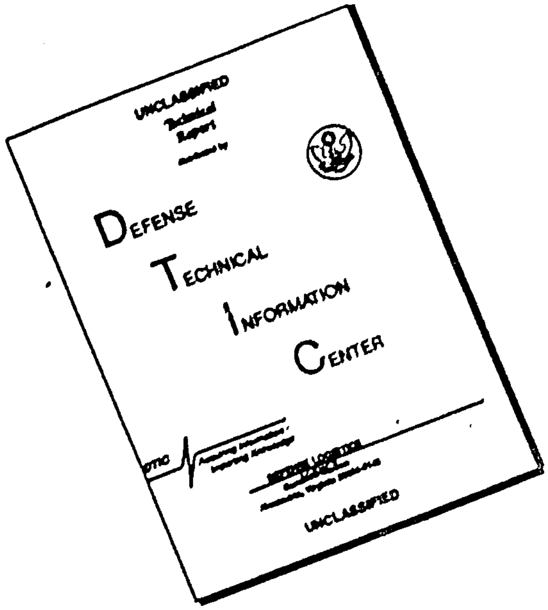

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CANOGA PARK, CALIFORNIA

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FINAL REPORT, STUDY OF O-RING AGING CHARACTERISTICS.

ROCKETDYNE

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CANOGA PARK, CALIFORNIA

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FOREWORD

This technical report was prepared under G.O. 8347 in compliance with Contract AF04(607)-7339, Part I, Paragraph A, Item 2 (CCN 10).

ABSTRACT

Presented are the results of an investigation made into several aspects of synthetic elastomer age deterioration to provide information for improved service-life estimates for liquid rocket engines.

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INTRODUCTION

Since 1957, Rocketdyne has been actively engaged in studying the aging of elastomers and compliant materials from liquid rocket engine systems. These studies have been directed toward the determination and recommendation of the service-life limits of these materials as used in liquid rocket engines for weapon system applications.

The current requirement to remove the soft goods from a rocket engine system after a service-life period of 42 months was established in 1957. This requirement results from the limited knowledge then available (Ref. 1) concerning the effect of aging on engine performance. However, it was recognized that the service life "might be extended as further history is obtained."

From past evaluations of soft goods conducted by Rocketdyne on Navaho, Redstone, Jupiter, Thor, and Atlas engine systems (Ref. 2) and from the general elastomer aging studies conducted by industrial and military organizations (Ref. 3 through 8), it appears that the service life of liquid rocket engine soft goods certainly exceeds the present 42-month service limitation and may extend to 5 or more years.

It is imperative that weapon system engines be in service as long as they may be capable of functioning reliably. Consideration of the high reliability requirements of weapon system rocket engines, and the time and costs involved in the dismantling of engine systems, primarily for the replacement of "aged" soft goods (after a 42-month service life) provides impetus to determine the maximum service life of these goods.

Although efforts have been made to study these problems, studies for obtaining fundamental, practical, O-ring aging information have not been performed. Furthermore, during previous evaluations of soft goods, numerous problem areas, requiring further investigation, have been uncovered.

The objective of this program was to provide a portion of the experimental and theoretical information deemed necessary for the formulation of recommendations of a service-life limit on O-rings in liquid rocket engine applications.

SUMMARY

An investigation has been made into several aspects of synthetic elastomer age deterioration to provide information for improved service-life estimates for liquid rocket engines. An extensive literature survey revealed a number of deficiencies in prior studies, including the fact that very little work had been done on the aging of Buna-N compounds. Buna-N O-rings, which are used extensively in military equipment, were used exclusively in this program.

The sensitivity to aging of the physical properties of elastomers was studied in detail. Particular attention was paid to those properties which are most closely related to O-ring function. The O-ring data obtained on samples from three manufacturers were subjected to statistical analysis to detect any mathematical relationships between the variables considered. Good correlations of aging time with hardness, elongation, and 10% compressive stress were found, although the mathematical models used did not fit the data from all three manufacturers equally well.

The relationship of standardized laboratory aging procedures to natural aging was investigated. O-rings from each of the three manufacturers were aged at 212 F for periods up to 90 days; of this group, O-rings from one manufacturer gave good correlations with natural aging for 100% tensile stress and elongation. The lack of similar correlations for a second manufacturer is indicative of the wide variations encountered in the aging resistance of military specification O-rings from different qualified sources.

Another portion of the study verified the existence of small but detectable changes in O-ring properties resulting from cyclic exposure to cryogenic environments while under stress. Analysis of soft-goods from in-service engines indicated such changes might be occurring. It is postulated that these changes are the result of some unexplained plasticizer effect rather than crystallization of the elastomer structure.

Information storage and retrieval programs have been prepared for computer handling of data from aging studies and soft-goods analysis of in-service engines.

TECHNICAL DISCUSSION

Of the many and varied parts used in liquid rocket engine systems, perhaps the most widely used of the functionally important parts are O-rings. Basically, an O-ring is a torus or "doughnut" of resilient and elastic synthetic composition that has been molded and trimmed to extremely close tolerances, and has a small cross-section in relation to its diameter. The mechanism of O-ring sealing is basically effected by the distortion of its resilient, elastic material to fill the leakage path.

The successful use of O-rings depends upon an evaluation of the service conditions as well as the design requirements of an application. It is, therefore, just as important to select a material that has the right combination of physical and chemical properties needed to withstand the anticipated temperatures, pressures, etc., as it is to design the groove correctly and choose the right size for the assembly.

CONSIDERATIONS IN FORMULATING ELASTOMER COMPOUNDS

The materials used for producing O-rings are referred to as compounds since, in most cases, they are a blend of various ingredients designed to give the desired physical properties. In general, a compound will include the ingredients listed in Table 1. The table also shows the importance of each ingredient, typical ranges of their concentration in an elastomer formulation, and examples of the chemicals used. The number of available combinations of these basic materials is, of course, quite large, and new materials are being introduced continually to meet changing demands.

TABLE 1

INGREDIENTS IN AN ELASTOMER RECIPE

Ingredient	Range of Concentration (Parts by Weight)	Importance of Formulation	Examples of Ingredients
Elastomer Gum	100	To provide the basic properties required in the compound	Styrene rubber Nitrile rubber Butyl rubber Polychloroprene rubber Polysulfide rubber Silicone rubber Fluorinated rubber
Vulcanizing Agents	0.5 to 50.0	To effect a crosslinking process and produce a strong (tough) elastic material	Sulfur Metallic oxides Benzoyl peroxide
Accelerators	0.3 to 3.0	To increase the rate of cure, improve the physical properties, and improve the aging of the compound	Thiazoles Thiuram sulfides Thiocarbamates Aldehyde amines Guanidines
Accelerator Activators	Zinc Oxide: 2.0 to 10.0 Stearic Acid: 0 to 4.0	To initiate accelerator action	Zinc oxide Fatty acids Litharge Amines
Antioxidants and Antiozonants	0 to 3.0	To retard oxidation and ozone attack and its subsequent deterioration of the compound	Secondary amine types Phenolic types Phosphites

TABLE 1

(Continued)

Ingredient	Range of Concentration (Parts by Weight)	Importance of Formulation	Examples of Ingredients
Pigments and Reinforcing Agents	20 to 300	To improve properties, change the balance of properties, and lower the cost	Carbon blacks Zinc oxides Clays Whitings Silicates Titanium whites
Softeners	2 to 50.0	Used as: 1. Processing aids for un-cured stock 2. Softeners for cured stock 3. Plasticizers 4. Freezing-point depressants 5. Organic reinforcing agents 6. Extenders	Thiazoles Aromatic mercaptans Disulfides Petroleum types (aromatic oils, resins, waxes) Pine tar types Coal tar types Natural fats and oils Synthetic organic compounds

The selection of an elastomeric composition for O-ring applications is nearly always a compromise selection of properties to most closely approach the optimum. There are numerous factors involved in the selection of a suitable compound for an application, foremost among which is a consideration of the various fluids to be handled, the temperature range and pressures to be encountered, and an indication as to whether the application is static or dynamic.

One of the important factors, generally given only secondary consideration, has been aging resistance. Although the military O-ring procurement documents do require some demonstration of a compound's aging resistance, they are more concerned with temperature (both high and low) and solvent and chemical resistance. Futhermore, the accelerated aging, temperature, and duration often specified is not severe enough to cause any appreciable deterioration of the elastomer (Ref. 3). Under these conditions, there are no provisions for the realistic demonstration of aging resistance, and there are no requirements for even minimum aging resistance. Information is needed about aging to establish some of these parameters.

FACTORS IN THE AGING OF ELASTOMERS

All elastomeric materials are subject to degradative changes with time. These physical and chemical deteriorative changes that occur on exposure to air, heat, and light are collectively known as aging, and are of the utmost practical importance as the military strives to increase the service life and the reliability of rocket engines.

The aging and degradation of elastomeric materials generally are believed to proceed as a result of concurrent aggregative processes (crosslinking, further linear polymerization, cyclization, branching) and disaggregative processes (scission, depolymerization). The crosslinking processes result in a three-dimensional structure of higher molecular weight and a hardened, brittle material of reduced extensibility. The scission-type aging process generally results in reduced chain length, and a softened, sometimes tacky material of lower molecular weight. A small percentage of these processes results from the continuing polymerization (curing) process and, as such, can be controlled by varying the curing conditions. However, the major percentage of the processes occur after the elastomeric compound is selected, formulated, and vulcanized, and are affected chiefly by the environmental conditions existing during the elastomeric part's service life.

The net effect of aging on any given compound is some weighted average of the aggregative and disaggregative processes. The relative rates of these reactions depend on many factors, some of them external to the rubber and some of them internal (Ref. 9). These factors are listed in Table 2. Many of these factors can and do interact in the aging process.

TABLE 2

EXTERNAL AND INTERNAL FACTORS IN THE AGING OF ELASTOMERS

External Factors	Internal Factors
Oxygen	Type of rubber
Pro-oxidants	Degree and type of vulcanization
Heat	Accelerator used
Ozone	Type of compounding ingredients
Fatigue	Processing factors
Light and weathering	Protective agents
Atomic radiation	

Considerable evidence has been collected suggesting that the attack of oxygen has a greater effect on rubber than any other degrading influence. In addition, the attack of oxygen is promoted by some of the other factors; i.e., heat which, of course, affects the rate of reaction as well as the mechanism of degradation. At very high temperatures, nonhomogeneous deterioration occurs as a result of a reaction rate of the material with oxygen exceeding the diffusion rate of the oxygen through the elastomer.

A small amount (1 to 2%) of oxygen in rubber renders it useless for most purposes. The oxidation of rubber is a complicated process, consisting of several reactions, each of which is influenced differently by the internal factors listed. The complexity of this process is illustrated by the fact that nearly all possible chemical functional groups involving oxygen have been found in oxidized rubber.

MECHANISM OF AGING

Investigators (Ref. 9 through 11) generally have agreed that the initial stage in the process of aging is probably the formation of a hydrocarbon-free radical by abstraction of a hydrogen atom somewhere along the polymeric chain. This may occur either by the action of a free radical left over from the polymerization process, or by the direct action of oxygen. Light, acting on a photosensitive molecule, also can produce a radical fragment that can be transferred to the polymer chain by abstraction of a hydrogen atom.

A polymer free-radical, R·, whose active odd electron can be anywhere along the polymer chain will, in general, readily add O_2 when it is present to give an $RO_2\cdot$ radical. The $RO_2\cdot$ radical also may undergo a chain-transfer reaction with an inactive portion of a polymer chain by abstracting a hydrogen atom to form the hydroperoxide, ROOH, and leave behind another radical of the type, R·.

These three active species, $R\cdot$, $RO_2\cdot$, and ROOH, are believed to be responsible for a large share of the deteriorative processes which have been termed as aggregative and disaggregative reactions. Mechanisms for these processes have been proposed in the literature and are listed in Table 3

TABLE 3

SUGGESTED MECHANISMS FOR AGGREGATIVE AND DISAGGREGATIVE PROCESSES

Aggregative Processes

$$R\cdot + \cdot R \longrightarrow R-R \qquad (1a)$$

$$R\cdot + R{=}R \longrightarrow R-\underset{\underset{\textstyle R\cdot}{|}}{R} \qquad (1b)$$

$$R\cdot + \cdot OO\cdot \longrightarrow ROO\cdot \qquad (1c)$$

$$R\cdot + \cdot OOR \longrightarrow ROOR \qquad (1d)$$

$$ROO\cdot + \cdot OOR \longrightarrow ROOR + O_2 \qquad (1e)$$

$$ROOH + R{=}R \longrightarrow \underset{\underset{\textstyle O}{\backslash\,/}}{R-R} + ROH \qquad (1f)$$

Disaggregative Processes

$$--CHX\cdot CHCHXCH_2-- \longrightarrow --CHXCH{=}CHX + \cdot CH_2-- \qquad (2a)$$

$$--CHXCH_2CHXCH_2OO\cdot \longrightarrow --CHXCH_2\cdot + CH_2O + CHXO \qquad (2b)$$

$$--CHXCH_2CHXCH(OO\cdot)CHX-- \longrightarrow --CHXCH_2\cdot + CHXO + CHOCHX \qquad (2c)$$

$$--CHXCH(OOH)CHXCH_2-- \longrightarrow --CHXCHO + \cdot CHXCH_2-- + \cdot OH \qquad (2d)$$

Under certain conditions, some of these reactions are presumably more important than others. For example, reaction (2a) is probably most important at quite high temperatures where large-scale depolymerization takes place. At lower temperatures, degradative reactions probably involve oxygen more directly, as in reactions (2b), (2c), and (2d). The relative rates of aggregative and disaggregative reactions depend, in general, on the chemical nature of the polymer and upon the conditions of aging (Table 2). For example, methyl side groups appear to favor scission, and carbon-carbon double bonds in the hydrocarbon chain favor crosslinking.

ANTIOXIDANTS

To protect against the deteriorating influences of oxidation, antioxidants often are incorporated into compounds. Antioxidants function by interrupting the chain reaction (as described previously) involved in the oxidation of the polymer and stopping the autocatalysis. This may be accomplished either by terminating free radicals or decomposing the peroxides into harmless products. Actually, antioxidants function by doing just this. A simplified picture (where the symbol "A" represents the antioxidant) is as follows:

$$R\cdot + AH \longrightarrow RH + A\cdot$$

$$ROO\cdot + AH \longrightarrow ROOH + A\cdot$$

$$RO\cdot + AH \longrightarrow ROH + A\cdot$$

$$ROOH + AH \longrightarrow \text{harmless fragments}$$

RELATIVE AGING RESISTANCE OF ELASTOMERS

In considering aging resistance, some elastomers are inherently more stable chemically than others. Butyl rubber, which is practically saturated, and neoprene, which is chlorinated, generally are more resistant to attack by heat, light, and oxidants than natural (Hevea) rubber, butadiene-styrene (Buna-S) and butadiene-acrylonitrile (Buna-N).

Generally, the greater the amount of unsaturation in the polymer, the more susceptible it is to aging. However, in the selection of elastomeric materials for various uses, age resistance is only one of a number of considerations to be weighed. For example, fluoroelastomers (such as duPont's Viton), which have outstanding aging resistance, are deficient in other properties, such as low-temperature resistance and compression set, thus limiting their use.

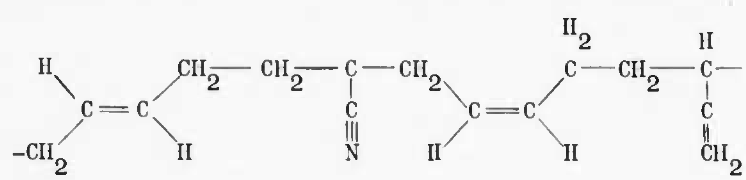
BUTADIENE-ACRYLONITRILE ELASTOMERS

Of the many available elastomeric materials used in O-ring service, the one most widely used in LOX/RP-1 rocket engine systems, and the one with which this study will be concerned, is butadiene-acrylonitrile (Buna-N, nitrile, NBR). Buna-N elastomer is used in many military specification compounds because of its good oil resistance, its relatively low compression-set properties, and its generally good over-all physical and chemical properties.

Basically, nitrile rubber is a copolymer (polymer chains obtained by polymerizing a mixture of two monomers) of butadiene and acrylonitrile. It has an irregular chain structure and, therefore, will not crystallize on stretching. In considering its chemical structure, the butadiene units are in the chain both in the 1,4 addition and 1,2 addition units. The

1,4 addition units are mostly in the trans configuration. The acrylonitrile units are in a random distribution in the chain and, of course, the ratio of butadiene units to acrylonitrile units depends on the ratio of monomers charged to the reactor.

An idealized segment of the nitrile rubber chain might look as follows:



trans - 1,4 butadiene　Acrylonitrile unit　Cis - 1,4 butadiene　1,2 butadiene

The average molecular weight is generally about 300,000. Since butadiene has a molecular weight of 54, and acrylonitrile has a molecular weight of 53 (nearly equal), their proportions by weight and molar proportions are practically the same.

The ratio of monomers in commerical nitrile rubbers varies from approximately 60% butadiene/40% acrylonitrile (high oil resistance but poor low-temperature properties) to 75/25 (medium oil resistance) to 85/15 (fair oil resistance and improved low-temperature properties). The acrylonitrile group makes the polymer polar and, therefore, resistant to nonpolar hydrocarbon solvents.

In selecting a nitrile composition for military O-ring specifications, a compromise generally is effected between compounding for maximum oil resistance (high-acrylonitrile polymer) and compounding for low-temperature flexibility (low-acrylonitrile polymer). Thus, many of the military O-ring compounds contain approximately 20 to 25% acrylonitrile in the polymer.

Because of the relatively low amount of saturation in the structure of the nitrile elastomer, it is susceptible to oxidation by the major external factors listed previously. Nitrile rubber, if made and used without antioxidant, deteriorates rapidly, especially in the presence of certain metallic impurities of peroxides. To overcome this difficulty, "shortstops" usually are added to the latex in the normal course of manufacture of the gum to destroy radicals and traces of peroxides, and antioxidants are incorporated in the final compounding to protect against other deteriorating influences.

The extent of the aging of nitrile rubbers may be controlled by varying the type and percentages of compounding ingredients, such as antioxidants, as well as the cure conditions. Again, however, emphasis must be placed on the fact that any particular elastomer formulation is based on a compromise selection of compounding ingredients to meet a particular application.

SUMMARY

Aging problems cannot be simply and easily disposed of by adding a magic ingredient to the elastomer compound. Detailed studies must be made to determine which of many complicated and probably interrelated variables have to be controlled to reduce the degree of aging to predetermined acceptable levels and, at the same time, maintain the required physical properties.

Although many investigators have conducted studies on the effects of aging on elastomers, few were concerned with O-ring aging in particular. And of these few, none were exclusively studying the problem as it pertains to nitrile rubber O-rings in rocket engine system applications.

This study of the aging characteristics of O-rings in liquid rocket engine systems was divided into five major tasks, each of which covered a particular set of problems. These tasks are listed as follows:

Task 1--Literature Search

Task 2--Study of O-Rings in Cryogenic Systems

Task 3--Evaluation of the Sensitivity of Various Properties to Aging

Task 4--Correlation of Accelerated Aging and Natural Aging

Task 5--The Mathematical Approach to the Analysis of O-Ring Aging Data

TASK 1--LITERATURE SEARCH

An extensive literature search has been conducted to study the work performed by other investigators in the field of aging studies. This was performed to permit Rocketdyne to build up from the foundation laid by previous investigators in particular areas, and to explore other areas opened by and introduced by these investigators.

The bibliography contains references mainly on the aging of elastomers and, particularly, of nitrile rubber. Included also are references to investigations on the behavior of elastomers and plasticizers under low-temperature conditions. These latter references were included because of interest generated in these subjects during the performance of Task 2 (Study of O-rings in Cryogenic Systems) of this program.

The literature search has included books, reports, and periodical literature. The following main sources were consulted:

- Applied Science and Technology Index, 1955 to mid-1962
- Chemical Abstracts, 1947 to mid-1962
- Engineering Index, 1951 to 1960
- Pacific Aeronautical Library Uniterm Index, 1955 to mid-1962
- Rocketdyne Library Catalog
- Technical Abstract Bulletin (ASTIA), 1953 to mid-1962

In addition, references contained in the researched literature, where pertinent, were also investigated.

The literature survey is arranged in alphabetical order either by author (where an author is known), technical organization, or periodical source responsible for the article.

Because of the extensive literature available on the subject of aging, and because of the unavailability of certain articles, some of the literature has not been abstracted. However, a listing of author, title, and source of information of such literature is included where it appears, based on title, that the literature would be informative and useful.

The abstracts have been prepared by Rocketdyne or by the author. Comments and evaluations are included for many of the articles. Wherever applicable, the Armed Services Technical Information Agency (ASTIA) document report number is included.

In reading the literature on the aging of elastomers, it becomes immediately apparent that the same type of elastomer may be designated by any one of several names, abbreviations, and/or initials. A listing of the terms that may be used for elastomers are provided in Table 4 . This reference table is included to simplify the reading of the literature abstracts, which generally refer to the elastomer designations used in the original article.

American Society for Testing and Materials

"Symposium on Aging of Rubbers," ASTM Special Technical Publication 89, March 1949. Chapters cover:

1. Mode of Attack of O_2 on Rubber
2. O_2--Absorption Methods--Their Utility and Limitations in the Study of Aging

TABLE 4

REFERENCE TABLE OF ELASTOMER NOMENCLATURE

Chemical Name	ASTM Designations	Commonly Used Names and Trade Names
Butadiene-Acrylonitrile	NBR	Nitrile, Buna-N
Styrene-Acrylonitrile	SBR	GR-S, Buna-S
Polybutadiene	BR	
Isoprene Rubber (synthetic)	IR	Synthetic natural rubber
Isoprene Rubber (natural)	NR	Hevea rubber
Polychloroprene	CR	Neoprene (du Pont)
Acrylate-Butadiene	ABR	
Isobutylene-Isoprene	IIR	Butyl, GR-I, Vistanex (Farben, Germany)
Vinylidine-Fluoride and Hexafluoropropylene Copolymer	FPM	Viton (du Pont), Fluorel (MMM)
Ethylene-Propylene Copolymer	EPM	EPR
Chlorosulfonyl-Polyethylene	CSM	Hypalon (du Pont)
Polychlorotrifluoroethylene Vinylidine Fluoride-Copolymer	CFM	Kel-F (MMM)
Silicone Elastomers (having only methyl-containing groups on polymer chain)	Si	
Polysulfide		Thiokol (Thiokol)
Polyurethane		Genethane (General) Adiprene (du Pont) Estane (B. F. Goodrich)

3. Chemical Δ's in Elastomers and Anti-Oxidants During Aging
4. Physical Aspects of the Aging of Rubbers
5. Effects of Light and Ozone on Rubber
6. Effect of T on Air Aging of Rubber Vulcanizates

This is an excellent monograph on the subject.

Beatty, J. R., and J. M. Davies: "Time and Stress Effects in the Behavior of Rubber at Low Temperature," Journal of Applied Physics, Vol. 20, 533-539, June 1949.

The stiffening of rubber-like materials at low temperature involves several different phenomena, sometimes with their effects superimposed. One of these is crystallization. This is a rate process which is generally very fast at high stresses and very slow at zero stress. In these experiments at temperatures near -25 C and under a shear stress of approximately 148 psi, the dynamic modulus of the rubber increased at a rate convenient to study. Correlation with X-ray data showed that crystallization was very likely responsible for the increase in stiffness. The rate of change of stiffness increased rapidly with increase in applied stress, and there was no optimum rate at -25 C as has been found for unstressed rubber. The degree of vulcanization influenced the rate of change--tighter cures giving smaller changes. Neoprene FR, GR-S and polybutadiene, which ordinarily show little evidence of crystallizations,showed very definite but small increases in stiffness. Mixing GR-S with natural rubber seems to limit the crystallization of the natural rubber rather effectively but, apparently, neoprene FR does not mix intimately enough with natural rubber to affect the crystallization of the latter appreciably.

Unfortunately, the authors do not discuss NBR.

Beatty, J. R., and A. E. Juve: "Stress Relaxation in Compression of Rubber and Synthetic Rubber Vulcanizates Immersed in Oil," India Rubber World, Vol. 127, 357-62, December 1952.

Stress relaxation in compression in air has been studied for compounds of various polymers. However, rubber seals, gaskets, and other applications are widely used where swelling agents such as oil are encountered. It was thought desirable to measure the stress relaxation properties of various rubbers (Buna-N, SBR, natural rubber, neoprene) to determine their performance under such conditions. The results show that continuous stress relaxation is inhibited by the presence of oil, and that unconfined swelling measurements directly predict the degree of inhibition. The variable of temperature and types of oil also were investigated.

The practical implications of this study are that rubber compounds that swell in the presence of oil have a property which may be utilized in some applications where it may serve a useful purpose. Examples are: O-ring seals and other types of gaskets where the rubber is used in compression. In these cases, the stress decays more slowly with time and, in some cases, the force would increase and the tendency for leakage would be minimized. In these experiments, the sample was relatively unconfined except for the direction of loading with only low frictional forces, which tended to prevent increase in volume. It was noted that with natural rubber and SBR at 70 C, the stress reached a maximum between 1,000 and 10,000 hours, which is a result of the sample reaching equilibrium with respect to swelling by the oil, and the stress then decreases, depending on the oxidative scission of bonds, in the same manner as found for tests conducted in air.

Berg, R. J.: A Review of Seal Materials for Guided Missile Applications, California Institute of Technology, Jet Propulsion Laboratory Progress Report 20-340, AD 163020, March 1958.

Bergstrom, E. W.: Aging of Unstressed Elastomeric Vulcanizates During Outdoor and Controlled Humidity Exposures, Rock Island Arsenal, AD203551, July 1958.

Report covers: (1) results of 7-year humidity aging program for various types of compounds (effect of humidity was found to be insignificant), (2) 6-year outdoor aging program (effect was determined after each year of aging). Tabulated results are presented. GR-S was affected more by outdoor aging than other types, and isobutylene/isoprene were least affected.

Bergstrom, E. W.: Indoor and Outdoor Aging of Elastomeric Vulcanizates Over a Ten Year Period, Rock Island Arsenal Laboratory, Report 61-3868, October 1961.

The properties of styrene/butadiene, chloroprene/isoprene, butadiene/acrylonitrile and isobutylene/isoprene vulcanizates, aged indoors and outdoors over a period of 10 years, were determined. It was found that the chloroprene/isoprene, butadiene/acrylonitrile and isobutylene/isoprene vulcanizates aged more outdoors than indoors. The butadiene/styrene vulcanizates aged approximately the same amount, both indoors and outdoors. The isobutylene/isoprene vulcanizate exhibited the least amount of aging, both indoors and outdoors.

The low-temperature-stiffness properties of all the vulcanizates that were aged indoors remained virtually unchanged after 10 years.

Vulcanizates of each type of rubber were wrapped in kraft paper, polyethylene, and a vinyl-coated, aluminum-foil/asphalt-impregnated kraft paper laminate to determine whether the wrappings would protect the rubber from aging. Unwrapped control samples also were included in the study. The results showed that the wrappings made no significant difference in the aging of any of the vulcanizates except those prepared from the chloroprene/isoprene copolymer. The chloroprene/isoprene vulcanizates wrapped in the foil paper laminate retained their original physical properties better than the unwrapped unwrapped vulcanizates or vulcanizates wrapped in the other two materials.

Some correlation was observed between the properties of vulcanizates aged in an air oven at 158 F and vulcanizates aged indoors and outdoors over a 10-year period. However, it was found that an aging test conducted in an air oven at 158 F was not sufficiently severe to be considered an "accelerated" test.

Five-year indoor or outdoor storage is considered to be the maximum permissible for general purpose rubbers such as were evaluated in this study. It would be possible to extend this storage life by special compounding or by using specialty elastomers.

This is a very informative and useful report. According to the author, it should be realized that any correlation evolved is limited to the specific vulcanizates compounded for this study and not to SBR, CIR, NBR, and IIR vulcanizates in general, since age resistance depends to a large extent on the various compounding ingredients (especially the curing system) used in the formulation. The Arsenal staff offers the opinion that 212 F is a more realistic temperature than 158 F for an accelerated air-oven aging test. After 10 years on this program, the author writes that after evaluating numerous aging test programs, any effort to directly correlate accelerated aging tests with indoor and outdoor aging tests is "a futile and unrewarding task." This author, after 2 years of work in this field, sympathizes fully with Arsenal personnel.

Boyer, R. F.: "The Compatibility, Efficiency, and Permanence of Plasticizers," Journal of Applied Physics, Vol. 20; 540-552, June 1949.

This is an excellent background article.

An attempt is made to interrelate three important aspects of plasticizer behavior: (1) compatibility, or how much plasticizer can be added without causing phase separation, (2) efficiency, or how much a given amount of plasticizer lowers the brittle temperature of the compound, and (3) permanence, or how well a plasticizer is retained by the polymer on heat aging or solvent treatment.

Compatibility is discussed in terms of the Flory-Huggins theory of the thermodynamics of polymer solutions, which relates the activity of the plasticizer to its concentration in the polymer. Efficiency is measured by how the plasticizer lowers the melt viscosity of the polymer. An empirical relationship between efficiency and μ, the Huggins polymer-solvent interaction constant, is shown. Loss of plasticizer at elevated temperatures depend in part on the effective vapor pressure of the plasticizer, and in part on how rapidly diffusion of plasticizer from the interior of the sample replenishes that lost from the surface. From the fact that diffusion constant times viscosity is a constant, it is possible to correlate measured diffusion rates with plasticizer content and with plasticizer efficiency. A linear relationship is predicted, and found experimentally, between logarithm of the diffusion constant and the brittle temperature. In this sense, the more efficient a plasticizer is, the more rapidly it can diffuse out of the polymer and be lost. Consideration is given to the effect of plasticizer on electrical resistance and tensile strength. A preliminary discussion of polymeric plasticizers is presented.

Bradbury, E. J., et al.: "Aluminum Block Heater for Aging Rubber and Rubber Compounds at High Temperatures," Rubber World, Vol. 134, 872-6, September 1956.

Buist, J. M.: Aging and Weathering of Rubber, W. Heffer & Sons, Ltd., for The Institution of the Rubber Industry, Cambridge, England, 1956.
This is an excellent monograph on theory and practical effects of aging. It contains chapters on:

1. Oxidation of Olefins--includes discussion on the effect of storage on properties of raw and unvulcanized rubber
2. Normal Aging and Aging Accelerated by Metallic Catalysis, Thermal and Photo Activation--includes discussion of aging processes, shelf aging, heat aging, light aging, and humidity aging

3. Flexcracking and Atmospheric Cracking
4. Accelerated Aging Tests
5. Individual Containers: Inter-Laboratory Comparison of Accelerated Aging Tests
6. Additonal Methods of Assessing Aging--discusses oxygen absorption tests, stress relaxation and creep tests, and aging of rubbers immersed in fluids
7. Commercial Antioxidants

Clinebell, B. J.: "O-rings--An Annotated Bibliography," India Rubber World, Vol. 7, 74-8, October 1952.

This is a Bibliography of 89 articles and patents discussing the general use of O-rings, including design and performance information. It has an interesting one-page foreword by E. N. Cunningham of Precision Rubber generally discussing O-rings and their history and function.

Cox, W. L, Shelton, and J. Reid: "Effect of Sulfur and Accelerator Variation on Aging," I and EC, Vol. 46, 33-37, October 1954.

This publication covers some work performed under U.S. Army contract. The variable effect of cure upon aging of rubber stocks suggested a need for further study of the effect of different types and amounts of accelerator, and different sulfur concentrations, upon the rate of oxidation of vulcanizates and the resultant deterioration of properties.

The rate of oxygen absorption increases with increased sulfur concentration in both natural rubber and GR-S black stocks. Changes in tensile strength, modulus, and ultimate elongation, resulting from the absorption of a given amount of oxygen, are only slightly affected by changes in sulfur and accelerator concentrations. Consequently, low-sulfur stocks exhibit better aging resistance. A change in the nature of the accelerator may affect both the rate of oxidation and the change in properties brought about by a given absorption of oxygen. For example, Santocure-accelerated stocks oxidize at a lower rate than TMTD-accelerated stocks, and also exhibit a lower rate of change in tensile strength for a given amount of oxygen absorbed.

An increase in either sulfur or accelerator concentration affects the properties of the vulcanizate and the early stages of aging so as to give a stiffer stock with lower elongation, both initially and after the absorption of any given amount of oxygen. This is particularly evident with GR-S, and is a major factor in the aging of GR-S vulcanizates.

du Pont's Elastomer Department

"15-Year Shelf Aging Test of Neoprene," du Pont's Elastomers Notebook 102, October 1961.

Two main conclusions are reached in this report:

1. Neoprene couplings seemed softer and more "live" than natural rubber couplings.

2. The important property in these small flexible couplings is "spring rate" (inch-pound/degree of rotational displacement). A plot of results indicated that the natural rubber had stiffened approximately three times as much as the neoprene after shelf aging for 15 years. There comes a point in time when the advantages of natural rubber are lost because of neoprene's better resistance to degradation.

Dyson, A.: "Temperature Sensitivity of Plasticizer-Polymer Systems," Society for Chemical Industry Journal (London), Vol. 69, 205, 1950.

Edwards, F. H.: "Low Temperature Tests on Rubbers," Engineering, Vol 185, 113, 24 January 1958.

England, W. D., et al.: "Weather Aging of Elastomers on Military Vehicles," Rubber Age, Vol. 85, 622, July 1959; also, Rubber Chemistry and Technology, Vol. 32, 1143-54, October 1959.

Fong, H. S.: "The Relation of Batch Variability to Aging," Bulletin of the Sixth Meeting of JANAF-ARPA-NASA Solid Propellant Surveillance Panel, 77-88, 5-7 December 1961.

Greensmith, H. W.: "Rupture of Rubber VII. - Effect of Rate of Extension in Tensile Tests," Journal of Applied Polymer Science, Vol. 3, January-February 1960.

An autographic method is described for obtaining load-extension curves for ring specimens extended at various rates from 0.1 to 2000% per second. Tensile strength of filled vulcanizates passes through a maximum. Three temperatures were used.

Hall, G. L., F. S. Conant, and J. W. Liska: "Long-Term Aging of Elastomers Under Continuous Shear Load," India Rubber World, Vol. 129, 611-616, February 1954.

Describes test apparatus and program to determine creep and changes in modulus of load-bearing elastomers (such as motor mounts). Good data and discussion.

Hodgson, G. T., Jr., and W. T. MacLeish: R-2, A New Aging Parameter for Elastomers, Paper presented to ACS and CIC (Chemical Industries of Canada) Rubber Divisions, Toronto, Canada, 10 May 1963.

A new parameter, designated as the "R-2 Value," for the evaluation of elastomeric compounds is defined as the ratio of the initial stress to the stress retained after 2 minutes of relaxation for a specimen held at constant tensile strain. This is a measure of short-term stress decay effects which, until very recently, have been ascribed to purely viscous flow and so have been largely neglected.

Data is presented from an aging study on natural, SBR, butyl and ethylene-propylene rubber compounds in which R-2 values are compared with corresponding values of modulus, tensile strength, and elongation.

The R-2 data on SBR (which would be somewhat applicable to NBR O-rings) is reported to be inconclusive because of poor reproducibility.

It is interesting approach to the problem of providing a significant aging parameter. More work is necessary in areas of particular interest to the contractor and Rocketdyne.

Holloway, J. M: Effect of Shelf Aging on Mil-P-5516A O-Rings, Mare Island Naval Shipyard, Rubber Laboratory. USN Report No. 92-4, 92-6, 92-7, 92-15 (January 1963).

O-rings from Goshen Rubber and Linear, Inc., initially conforming to Specification MIL-P-5516A, have been shelf aged for 8 years. During the first 4 years of this period, the O-rings were stored in sealed, lined, envelopes. Representative samples then were tested for tensile strength, ultimate elongation, tensile stress, set, and specific gravity. During the latter 4 years, some were kept sealed in the envelopes, some were exposed to air and artificial light, and some were exposed to air with light excluded. Representative samples were tested again. No significant changes in the measured physical properties were observed. It is concluded that O-rings meeting the requirements of Specification MIL-P-5516A will give satisfactory service after at least 8 years aging at moderate temperature.

The data appear to be quite conclusive, and is the average of 40 rings (for tensile properties) in each yearly test.

Houwink, R. (Editor): Elastomers and Plastomers--Vol. I, General Theory, Elsevier Publishing Co., Inc., New York, 1950.

Includes very good discussions on molecular constitution, mechanical properties (including second-order transition effects and brittle point, effect of temperature and plasticizer and viscous-elastic phenomena), physics and structure (X-ray examinations of amorphous and crystalline rubber), and plasticizers. Vol. II--Manufacture, Properties, and Applications, 1949. Vol. III—Testing and Analysis, 1948.

Jordan, J.: "Thermal Expansion of Elastomers," Machine Design, Vol. 32, 144, 7 January 1960.

Short one-page article discusses tests performed to provide data for designers on the linear coefficient of thermal expansion. The data are presented in Table 5.

TABLE 5

LINEAR THERMAL EXPANSION OF TYPICAL ELASTOMERS AND COMMON ALLOYS

Compound Base	Contraction +75 to -65 F (in./ft)	Expansion +75 to +375 F (in./ft)	Coefficient of Expansion (in./in./deg F)
Nitrile, General Purpose	0.104	0.224	6.2×10^{-5}
Chloroprene	0.128	0.273	7.6×10^{-5}
Viton-A	0.130	0.277	7.7×10^{-5}
Kel-F	0.140	0.300	8.3×10^{-5}
Silicone	0.173	0.370	10.3×10^{-5}
Low-Temperature Type Silicone	0.183	0.392	10.9×10^{-5}
High-Temperature Type Aluminum 178-T	0.022	0.017	13.0×10^{-6}
Stainless Steel, Type 302	0.016	0.035	9.6×10^{-6}
Steel, Mild	0.011	0.024	6.7×10^{-6}
Invar	0.001	0.002	6.0×10^{-7}

Juve, R. D., and J. W. Marsh: "Low Temperature Behavior of Butadiene-Styrene Copolymers," Industrial and Engineering Chemistry, Vol. 41, 2535-38, November 1949.

Elastomers lose elasticity and tend to become stiff at low temperature. A study has been made of means of reducing the tendency for butadiene-styrene copolymer vulcanizates to stiffen during service at low temperature.

Compounding variables which affect the behavior at low temperature include type and amount of plasticizer, particle size of the carbon black, and extent of vulcanization.

In selecting a plasticizer for low-temperature applications, it is necessary to consider, in addition to low-temperature flexibility, the volatility and water extraction. Also important are the effects upon the processability and the physical properties of the rubber.

Juve, A. E., et al.: "The Effect of Temperature on the Air Aging of Rubber Vulcanizates," ASTM Bulletin, Vol. 195, 54-61, 1954.

Juve, A. E., et al.: "Effect of Temperature on the Air Aging of Rubber Vulcanizates," Materials Research and Standards, Vol. 1, 542-5, July 1961.

Kallas, D. H.: Investigation of Shelf Aging of Synthetic and Natural Rubber Materials, U.S. Navy Materiel Laboratory, New York Naval Shipyard, Report 5974, AD229186L, December 1959.

A three-section report summarizing test procedures for artificial aging. The 140 F Geer Oven Aging Method was used. Parameters studied included tensile strength, % elongation, 300% tensile modulus, swelling ratio, compressive set, and stress relaxation of packaged and unpackaged samples. Unfortunately, compound numbers were used and, in many cases, the type was not specified. Graphical data is very good, but not too usable without identification.

King, W. H., and R. E. Harding: Evaluation of Compression Set of Vulcanized Elastomers--Standard Versus Variable Deflection Methods, ASTM S.T.P. No. 311, 1962.

Reports the results of investigations involving a comparison of two testing techniques for measuring the compression set of vulcanized elastomers--the recently changed method of variable deflection (dependent on hardness), and the newer method involving a uniform deflection of 25% (regardless of hardness).

The tests indicate that there is no difference between the two methods that cannot be attributed to random variation. Compression set tests using 25% deflection was adopted, since it is believed to simplify and facilitate the compression set tests.

Leyland, B. N., and R. L. Stafford: "Aging of Rubber: Effects of Metal Contamination," Transactions of the Institution of the Rubber Industry, Vol. 35 No. 2, April 1959.

An interesting article for rubber manufacturers. The oxidation of raw rubber is strongly promoted by small amounts of copper (30 to 100 ppm) especially when this is introduced as the salts of weak organic acids. There is evidence that these salts act as pro-oxidants, increasing the rate of oxidation, but not changing the nature of the oxidative reaction. Attention is drawn to the pro-oxidant activity of iron in the form of ferric stearate. Although not so active as copper in raw rubber, it certainly could be a source of serious degradation. Investigation of the inhibition of the metal-catalysed oxidation of raw rubber emphasizes the effectiveness of zinc diethyl dithiocarbamate (ZDC) and tetramethyl thiuram disulphide (TMT) against copper contamination. It also is shown that a nonstaining inhibitor, originally developed for vulcanized compounds, is effective in affording inclusive protection against both copper and iron in raw rubber.

In sulphur-vulcanized compounds, the pro-oxidant activity of copper and iron is again demonstrated, the relative effects being smaller the greater the oxidizability of the uncontaminated control compound. In these compounds, ferric stearate is shown to be as potent as copper stearate in promoting degradation. Although a few conventional antioxidants give fairly good protection against copper contamination in vulcanized rubber, there is a need for even more powerful metal inhibitors that are also good conventional antioxidants. The synergism of selected antioxidants with mercaptobenzimidazole (MBI) is demonstrated in copper-contaminated compounds, leading to the design of improved inhibitors. Some characteristics of a nonstaining inhibiting system of this type are discussed, including its effectiveness in both raw and vulcanized rubber; this affords a means of conferring protection against metal contamination both before and after vulcanization. It is shown that the efficacy of such a system in vulcanized compounds is not restricted to high-temperature oxidation, but that it is also effective in the region of room temperature.

Sulphurless TMT vulcanized compounds are shown to be strikingly different in their reaction to metal contamination. In such compounds, copper stearate itself acts as a powerful antioxidant, whereas ferric stearate still remains markedly pro-oxidant in its effect.

Lichtman, A.: Investigation of Aging Tests for Tubes and Covers of Synthetic Rubber Hose, U. S. Navy Material Laboratory, New York Naval Shipyard Final Report, Laboratory Project No. 5776, AD 214403, August 1958.

Lichtman, J. Z.: Determination of Compressive Strength of Elastomers, AD226709, July 1959.

Six rubber mount stocks (CR, GRS, and NR) were evaluated under various compressive conditions. Compression deflection and recovery characteristics were determined at a specimen deflection of 0.200 inch (40%). Stress-strain curves are presented.

Lichtman, J. Z., and C. K. Chatten: "Physical Properties of Natural and Synthetic Rubber Materials at Low Temperatures," Analytical Chemistry, Vol. 24, 812-818, May 1952.

Good detailed paper on low-temperature testing. The authors , in an analysis of the manner of employing the major number of rubber items in shipboard low-temperature service, showed the following physical properties to be the most significant: (1) flexibility, or the magnitude of stress required to produce an observed degree of deformation; (2) compression set, including the rate and amount of dimensional recovery of a material after being held under constant deformation; and (3) brittleness or structural failure of a material under rapid deformation. Since the significance of these properties may vary from one application to another, the authors suggest that specifications of rubber for various applications would require the evaluation of the property or properties that are pertinent to the service performance of the material.

A review was made of the methods used in evaluating the three classes of properties. The second property, compression set, is usually evaluated after the specimens have been aged at elevated temperatures under constant deflection. A basically similar method has been adopted and standardized by the Navy for carrying out low-temperature evaluations, a modification being made in that the dimensional recovery of the specimen is evaluated at the test temperature and at two time intervals, i.e., 10 seconds and 30 minutes after the specimen is released from the clamping plates. In this manner, both the rate and amount of recovery of the specimen are evaluated, and the data so obtained can be used in differentiating between first-and second-order transition effects. The evaluation of the third property, brittleness, has likewise been more or less standardized, although there are a number of different instruments designed to conform to the procedural requirements.

A survey of all such equipment and methods was undertaken to standardize appropriate ones and to determine the degree of correlation in data obtained in the tests. A comparison of data derived in evaluating typical stocks exposed at low temperatures, and tests using a torsion-wire apparatus and a hardness indentation device, confirms the existence of a mathematical relationship between flexural modululus and hardness indentation. The investigations indicate the feasibility of using either instrument to evaluate the stiffness or the hardness properties of elastomers over a range of exposure conditions. The small T-50 type specimens used with the torsion-wire apparatus are well adapted for use in evaluating changes in stiffness of elastomers due to exposing the materials to solvents.

Lyubchanskaya, L. I., et al.: "Degradation of Main Chains and Crosslinks in the Aging of Vulcanizates," Rubber Chemistry and Technology, Vol. 34, 922-4, July 1961.

McCuistion, T.: "O-Rings--Cure Date and Control," Applied Hydraulics, Vol. 10, 114, April 1957.

Brief and not particularly illuminating explanation of ANA 427 Age Control specification.

Mandel, J., F. L. Roth, M. N. Steel, and R. D. Stiehler: "Measurement of the Aging of Rubber Vulcanizates," Journal of Research of the National Bureau of Standards, Vol. 63C, No. 2, October-December 1959.

An excellent study and report. The authors report that a study of aging data in the literature and of measurements made at the National Bureau of Standards indicates that ultimate elongation is the best of the tensile properties for characterizing the deterioration of rubber vulcanizates during storage at various temperatures. Ultimate elongation (strain at failure) decreases during aging for all types of rubber vulcanizates; whereas, tensile strength and modulus may increase, decrease, or remain essentially unchanged.

This study includes measurements of ultimate elongation of a nitrile rubber vulcanizate after various periods of storage at temperatures of 23, 34, 45, 57, 70, 85, and 100 C. It also includes a study of the published data on ultimate elongation obtained in an interlaboratory test conducted by Subcommittee 15 of ASTM Committee D-11, involving vulcanizates of five different rubbers stored at 25, 70, 100, and 121 C.

The change in ultimate elongation over prolonged periods of storage cannot be expressed by a simple mathematical equation. However, during most of the useful storage life of a rubber vulcanizate, the elongation decreases approximately linearly with the square root of time. The data indicate that for some vulcanizates an estimate of storage life at room temperature can be made from measurements of ultimate elongation at two or more elevated temperatures.

Mark H., and G. S. Whitby (Editors): Advances in Colloid Science--Vol. II; Scientific Progress in the Field of Rubber and Synthetic Elastomers, Interscience Publishers, Inc., New York, 1946.

An excellent (but somewhat dated) theoretical background text of rubber technology. Includes chapters on the following subjects:

1. Second-Order Transition Effects in Rubber and Other High Polymers
2. Crystallization Phenomena in Natural and Synthetic Rubbers
3. The Study of Rubberlike Substances by X-Ray Diffraction Methods
4. The Thermodynamic Study of Rubber Solutions and Gels
5. Significance of Viscosity Measurements on Dilute Solutions of High Polymers
6. The Kinetic Theory of Rubber Elasticity
7. Vulcanization
8. Rubber Photogels and Photovulcanizates
9. Reinforcing and Other Properties Compounding Ingredients

Materials and Methods Staff Report

"Specifying Elastomers for Low Temperature Service," Materials and Methods, Vol. 38, 114-118, November 1953.

A very good general discussion on what happens to elastomers at low temperatures (~ -60 F), how common elastomers differ in their low-temperature behavior, and how they can be altered to meet specific low-temperature conditions.

Maurer, J. E.: Five-Year Summary of the Firestone Case-Aging Contract, U. S. Army, Rock Island Arsenal Laboratory Report 53-2371, AD 14212, 15 June 1953.

Mayo, F. R., J. Heller, and J. L. Klinck: Accelerated Deterioration of Elastomers, Stanford Research Institute, First Quarterly Progress Report, AD-288 642, November 1962.

The object of this program is to find methods to accelerate the deterioration of elastomers at or near ambient temperatures. Catalysis of antioxidation is said to be the most promising approach. The study is concerned with cis-polyisoprene (natural rubber).

The premises, the basic problems, and the first approach in this research are set forth. A benzene solution of polyisoprene is rapidly degraded by oxygen in the presence of 2, 2-azobis- (2-methylpropionitrile), but not in its absence. Cobaltous stearate has little effect on the initial stages of oxidation. Dimethylcadmium causes crosslinking and initiates oxidation of polyisoprene, possible by acting as a source of methyl radicals. Quantitative comparisons are lacking and will be sought.

Mesrobian, R. B., and A. V. Tobolsky: "Some Structural and Chemical Aspects of Aging and Degradation of Vinyl and Diene Polymers," J. of Polymer Science, Vol. 2, 463-487, 1947.

A highly theoretical discussion of basic concepts of aging of polymers. The chemical reactivity of vinyl and diene polymers manifested during aging and degradation is similar to the reactivity manifested during polymerization; namely, the activated intermediates are radicals and the reaction proceeds by a chain mechanism. A discussion of the possible types of aggregative and disaggregative processes involved in aging is presented. On the basis that polymerization and degradation occur by means of the same radical mechanism, experimental evidence is given to indicate that under certain conditions both reactions may occur simultaneously. Viscosity changes of solutions of mono- and polystyrene and methyl methacrylate were studied under varying conditions of heat, oxygen, catalysts, light, and photosensitizers. An analysis of the concurrent aggregative and disaggregative reactions involved in aging may be obtained by isolating one reaction from the other, either by various physical methods, such as intermittent and continuous stress relaxation, or by such classical methods as sol-gel determinations and aging in solution. A comparative study of the rate of oxygen absorption of a large number of polymer types was undertaken to evaluate the factors affecting oxidation. Evidence is presented to show that these factors may be specified by the following: (1) chemical structure of the polymeric material, (2) presence of antioxidants, and (3) compounding and vulcanization. The oxidizibility of polymeric materials was also studied in a circulating oxygen absorption apparatus to determine the effect of evolved, gaseous oxidation products. A preliminary study of the effect of light on the aging of butyl and GR-S rubber, as measured by oxygen absorption and stress relaxation, is presented.

Morris, R. E., J. W. Hollister, and P. A. Mallard: "The Cold-Compression Sets of Natural and Synthetic Vulcanizates," Rubber Chemistry and Technology, Vol. 19, 151-162, 1946.

Describes an apparatus and procedure for the cold compression-set testing of elastomers. The procedure is a modification of the standard ASTM test for hot compression-set, method B (40% deflection). Cold compression set was found to be a reversible phenomenon. For noncrystallizable rubbers, the compression set is of transitory nature even at low temperatures.

Morris, R. E., J. W. Hollister, and A. E. Barrett: "The Cold Compression Set of Elastomer Vulcanizates," Industrial and Engineering Chemistry, Vol. 42, 1581-7, August 1950.

An informative paper on the significance of the cold compression set of elastomers (natural rubber, SBR, nitrile, neoprene). Cold compression set is caused by slow rate of recovery due to high internal viscosity, and also may be caused by crystallization or by second-order transition if conditions are favorable for either of these phenomena. The cold compression-set test is advocated for use to determine the sealing ability of gaskets for low-temperature service (~ -35 F).

Morris, R. E., and J. W. Hollister: "Plasticizers for GR-S Gasket Stocks to be Used at Low Temperatures," Rubber Age, Vol. 70, 195, November 1951.

The effects of low-temperature on GR-S (increased hardness and stiffness and decreased resilience) can be mitigated by compounding with plasticizers. Since cold compression set correlates with the sealing ability of a gasket at low temperatures (according to previous work), this test was selected as the screening test for evaluating plasticizers with GR-S.

The best plasticizers for reducing the cold compression set of GR-S (SBR) at -35 F have been selected from a total of 181 plasticizers. The best plasticizers were further tested in a GR-S stock for volatility and extractability by water. Several GR-S stocks containing different plasticizers, and a similar stock containing no plasticizer, were checked for compression set at -60, -30, 0, and +30 F after various recovery times. It was found that all of the stocks tended to recover from compression even at -60 F, and that the relative benefit of the plasticizers was not the same at the different temperatures.

Mortensen, R., et al.: Aging of Cure Dated Items and Various Elastomeric Compounds, University of Oklahoma Research Institute, AD 282-230, 31 January 1962.

This report summarizes work performed under an Oklahoma City Air Materiel Area contract. Although the title indicates concern for aging of cure-dated elastomer, the 11 phases have little pertinence with the title subject. Most of the pertinent topics concern work performed by investigators other than the authors. The data obtained by the authors on temperature retraction studies is of little value because of a limited number of samples in each of several widely divergent categories, that were all compared on a common basis. An extensive bibliography covers almost every possible aspect of elastomer chemistry, testing, aging, compounding, etc., as well as many other fields of endeavor. The extent and nonselectivity of the bibliography makes it of little use.

Topics covered include:

1. Correlations between Natural and Accelerated Aging and Mechanical Properties
2. Vapor Phase Swelling
3. Vapor Phase Swelling Studies with the Quartz Beam Microbalance Apparatus
4. Vaporization of Volatile Components in the Rubber
5. Neutron Irradiation of Rubber
6. Swelling Behavior under Stress Conditions
7. Removal of 1010 Oil from O-Rings

8. Leaching of Constituents from O-Ring
9. Temperature Retraction Apparatus
10. Literature Bibliography

Morton, M.: Introduction to Rubber Technology, Reinhold Publishing Corporation, New York, 1959.

An excellent reference text on rubber technology. The chapter on physical testing (by A. E. June) is particularly interesting and informative. Other worthwhile chapters of interest include:

Introduction to Polymer Chemistry

Rubber Plasticizers

Antioxidants and Antiozonants

Nitrile and Polyacrylate Rubbers

Murfitt, H. C.: "Plasticizers for Use at Extremes of Temperature," British Plastics, Vol. 35, 510-15, October 1962.

Murray, K.: Investigation of Oil Aging Procedures for Elastomeric Materials, WADC Report 58-18, ASTIA No. 151.

Several oil aging procedures utilizing various venting methods, and an oven or an aluminum-block heater as heat sources, were compared to determine the most suitable reproducible test procedures for evaluating potential oil-resistant elastomers at elevated temperatures.

The "chimneyed-stoppered" tube method, as described, provides for better reproducible results.

NASA-Marshall Memo, Inspection of Juno II Vehicle 0-Ring, 26 September 1960. (Unpublished)

Discusses examination of 0-ring gaskets taken from valves removed from Jupiter missile 19-D. A recommendation is made that the installed life of rubber gaskets in Juno II type missiles be extended to 36 months. They also suggest that the condition of the lubricant be evaluated as a function of time along with 0-rings.

Nash, H. L., and L. G. Wilson: An Instrument for the Measurement of Stiffness of Elastomers at Low Temperatures, Defense Research Chemical Laboratories (DRCL) Report No. 360, Defense Research Board of Canada, December 1961.

A description is given of an instrument developed at DRCL for measuring the changes in stiffness of elastomers over the temperature range from room temperature to -100 C.

Results obtained for many elastomers are detailed, together with a discussion of the practical significance of the stiffening point.

From graphs of the force necessary to bend a sample around a cylindrical mandrel with known radius of curvature vs temperature (+20 to -60 C), the observation is made that:

1. The force needed to bend the material through a given angle is dependent not only on the material, but also on the geometry of the specimen.
2. The temperature at which rapid stiffening occurs is not always a well-defined temperature.

Nosov, Y. A., and I. I. Farberova: "Methods of Evaluating Rubber Used In the Manufacture of Sealing Units," Soviet Rubber Technology, Vol. 18, 36-41, April 1959.

A basic review article covering the methods used for evaluating rubber used in the manufacture of seals, and methods of control testing the latter. It emphasizes the advisability of incorporating into specifications indices which reflect more accurately the conditions in which seals work (e.g., the contact pressure exerted by the rubber). The authors suggest the use of compressive property testing of rubber for sealing units. These include compression set, compressive-deflection, and compressive stress decay.

Offner, R. E.: Cooperative Laboratory Stiffness Measurements of Rubber at Low Temperatures, U. S. Army, Rock Island Arsenal Laboratory Report 54-1148, AD 33585, March 1954.

Ossefort, Z. T.: <u>Accelerated Heat and Oxygen Aging of Rubber</u>, Rock Island Arsenal Laboratory, Report No. 55-1993, AD 66097, 18 May 1955.

A discussion is presented covering the following principal points in the aging of rubber:

1. Chief causes and effects of heat and oxygen aging of vulcanizates
2. Uses of oven aging tests
3. Some of the goals of the ordnance aging program
4. Test methods and apparatus used in studying aging of vulcanizates

Procedures used and results of several studies on some of the factors responsible for heat and oxygen aging of vulcanizates are reported. The specific areas investigated were the following:

1. Effects of type and amount of antioxidant on aging
2. Effect of varying the curing system on aging
3. Transference of compounding ingredients during air oven aging
4. "Nonsulfur" vs "sulfur" based curing systems in extended aging.
5. Effect of test media and apparatus on aging
6. Investigations of test methods and procedures and their effects on aging

Compounding ingredients may be transferred from one compound to another when they are aged simultaneously in the air oven. However, this factor assumes importance only in the case of extremely "age-sensitive" compounds such as those containing no antioxidant and based on an elemental sulfur curing system. In all other cases examined, if any transference effect was present it was so slight that it could not be detected.

The most important factor in compounding stocks for the retention of physical properties after extended air-oven aging was the type of cure used. The vulcanizates based on the nonsulfur cures were outstandingly better in age resistance than those based on elemental sulfur cures.

With the possible exception of oxygen under pressure, aging results were not greatly affected by the media or apparatus used in testing. This was true whether the medium was oxygen (atmospheric pressure), air, nitrogen, carbon dioxide, or vacuum, and for seven different types of apparatus.

Based on considering tensile strength (too erratic) and hardness (not sensitive and reproducible enough), the author states that the change in elongation at constant stress was the best test procedure for estimating the aged condition or qualities of elastomers.

One of the objects of the aging program conducted at this arsenal and under contract has been the development of a chemical or physical test which can be used in government specifications to ensure the procurement of rubber products having excellent age resistance. The best test which has been found, as is indicated in this work, is the measurement of changes in elongation produced by the aging process. It is considered that such a test should be incorporated into government specifications.

A program was under way to correlate the results of various accelerated aging tests with long term "natural" aging. Correlation exists to the extent that the nonelemental sulfur-cured compounds, which resist aging so well in accelerated tests, also resist the effects of long-term (5 years) natural aging both outdoors and indoors.

Ossefort, Z. T.: "Curing Systems for Improved Aging Resistance of Rubber Vulcanizates," Rubber World, Vol. 135, 867-75, March 1957; Vol. 136, 65-73, April 1957.

Ossefort, Z. T.: The Influence of Accelerator Residues on Age Resistance of Elastomeric Vulcanizates, U. S. Army, Rock Island Arsenal, Report No. 58-7474, AD 211559, 1958.

Owens, F. S.: "Stress Relaxation of Elastomers," Project 7021, Task 73656 WADD TR 60-922, Pt I, Wright Air Development Division, Wright-Patterson Air Force Base, Ohio, March 1961.

An intensive literature survey on elastomer stress relaxation revealed that previous investigators had been primarily concerned with the environmental effects of oxygen and temperature upon the rate of stress relaxation of elastomers rather than with the isolation of variables directly involved in the preparation of elastomeric vulcanizates. A systematic investigation of such variables as the milling time, vulcanization time, elongation rate, and the amounts of various compounding ingredients was therefore performed.

A medium acrylonitrile-content butadiene-acrylonitrile elastomer was utilized exclusively as the base elastomer for the vulcanizates of this investigation. A compounding formula was selected as the "standard" stock, and the effects of the amounts of individual compounding ingredients were investigated individually through variations from this formula.

In addition to the investigation of the stress relaxation characteristics of butadiene-acrylonitrile vulcanizates per se, it was also the intent of this program to utilize the procedures developed in continuing studies of vulcanizates of other elastomers. This continuing study will utilize elastomers of high thermal stability and will involve measurements of stress relaxation at high temperatures.

Perrott, W. O.: Determine Special Characteristics Of a Buna-N Rubber Stock, U. S. Army, Detroit Arsenal, Memo Rubber Progress Report No. 2534-B, AD 33284, 31 August 1953.

Pickett, A. G., and M. M. Lemcoe: Handbook of Design Data on Elastomeric Materials Used in Aerospace Systems, T. R. ASD-TR-61-234, AD 273880, Southwest Research Institute, January 1962.

The objective of this handbook is to provide aerospace weapons system design engineers with useful data on the materials properties of elastomers. The sources of this information are Department of Defense research reports and the technical literature of engineering design and elastomer technology. The elastomeric materials for which data are presented are compounds of high polymers currently available in the U.S.A. The properties considered are original mechanical and physical properties and the changes in these properties that result from aging and exposure to environments of aerospace weapons systems. Elastomer compounding is only briefly treated because the handbook is intended for use by structural and mechanical engineers rather than by rubber chemists and technologists. Elastomer part design methods are not reviewed because they are the subjects of other Department of Defense reports which this handbook is intended to complement. A selected bibliography of technical literature on elastomers and elastomeric parts is included to aid the handbook user who needs further information on these topics.

Pollack, L. R., R. E. McElwain, and P. T. Wagner: "Oxygen Absorption of Vulcanizates," Industrial and Engineering Chemistry, Vol. 41, October 1949, 2280-2286.

Rates of oxygen absorption have been measured for two natural and six synthetic rubber stocks (2-CR, SBR, NBR, butyl, and polysulfide). The course of aging in an oxygen bomb and in an air oven was followed by measuring the changes in tensile strength and ultimate elongation. The authors feel that the correlation between oxygen absorption rates and deterioration of physical properties is close enough to justify substitution of a rapid oxygen absorption measurement for longer standard procedures in evaluating aging characteristics of rubber stocks. However, it appears that the basis for correlation is rate of loss of tensile strength during oxygen bomb aging. Both the tensile change and oxygen bomb aging are no longer considered to be the most significant aging parameters and methods. The data do indicate that oxygen absorption can provide some measure of comparative aging information, and that it is an interesting aging criterion to explore further.

Pollack, L. R.: "Oxygen Absorption versus Conventional Aging of Commercial Vulcanizates," India Rubber World, Vol. 130, April, 1954, 53-57.

A series of commercial vulcanizates (natural, chloroprene, GR-S, and nitrile) were aged in the oxygen bomb, the air oven, and by an oxygen absorption test. The authors suggest that the oxygen absorption rate, because of the nature of the chemical reactions involved, provides a more fundamental evaluation of the oxygen aging of elastomers. Their correlations, as in a previous paper, relate to tensile loss rate in an oxygen bomb with oxygen absorption, and the same comments apply to this work as in the review of their previous paper.

Pollack, L. R.: "Aging Studies on Commercial Vulcanizates," Proceedings of JANAF Conference on Elastomer Research and Development, 1954, Publication No. 370, National Academy of Sciences, National Research Council, 1954, 72-75.

Pollack, M. A.: "A Low Temperature Flexibility Tester," Rubber Age, Vol. 69, 1951, 713-717.

Polmanteer, K. E., P. C. Servais, and G. M. Konkle: "Low Temperature Behavior of Silicone and Organic Rubbers," Industrial and Engineering Chemistry, Vol. 44, July 1952, 1576-1581.

In tests performed to evaluate the low-temperature properties of silicone rubbers, these rubbers were compared to natural rubber and SBR by means of modulus, torsional stiffness, and percent recovery data. A special cold chamber was designed for stress-strain measurements at temperatures as low as -130 F, below that attainable with dry ice.

Some types of silicone rubber did not stiffen appreciably until temperatures between -112 and -130 F were reached, whereas both natural rubber and SBR stiffened at -76 F. Careful control of the induction period in conjunction with the Gehman cold-flex apparatus showed that silicone rubber Type II may be supercooled, and crystallization is a rapid process.

The results of these tests indicate that silicone rubbers will perform satisfactorily in a low-temperature region for applications requiring an elastomer.

This paper reports on two types of silicone rubber stocks: Type I, which crystallizes at about -76 F, and Type II, which crystallizes at about -112 F. Type I is exemplified by Silastic 160, and Type II by Silastic 250 and 6-160.

The purpose of this paper is to describe briefly the special apparatus used in obtaining stress-strain curves at temperatures down to -130 F or below. The modulus data so obtained give a more complete picture of the behavior of silicone rubber at low temperatures. These data are compared with those for natural rubber and SBR determined on the same apparatus.

Radi, L. J. and N. G. Britt: "Fundamental Low Temperature Retraction Studies of Natural and Synthetic Elastomers," Industrial and Engineering Chemistry, Vol 46, November 1954, 2439-2444.

Various elastomers, including natural rubber, SBR, nitriles, neoprene, silicone, butyl, and polysulfide rubber, were permitted to retract at a constant temperature, and retraction was allowed to proceed at that temperature until an essential equilibrium existed between forces tending to deter and forces tending to retract the elastomer. The extent of deviation from a sigmoid or S-shaped normal curve of percent retraction vs temperature at which it occurs provides information concerning crystallization parameters and the low-temperature behavior of the elastomer. This is a valuable background article.

Rehburg, M. H.: "Evaluation of the Fueling and Aging Effects on the Thrust Unit of Redstone Missile 1007," Technical Report RPE-R1, Chrysler Corporation Missile Division, 22 February 1961.

Reinsmith, G.: "Aging and Preservation of Vulcanized Rubber-I and -II," India Rubber World, October 1947 (I) and November 1947 (II).

This is a dated and very general review of the factors affecting aging deterioration of vulcanized rubber, the methods for evaluating this, and means of preservation.

Rocketdyne Internal Reports:

MPR 3-252-507, Soft Goods Analysis of Jupiter Engine S/N CJ4501, 3 January 1963.

MPR 2-252-6, Evaluation of Soft Goods From Jupiter Engine S/N 4068, 19 September 1962.

TAMM 2114-608, Evaluation of Soft Goods From Launch-Ready MA-2 Engine Systems, 18 June 1962.

TAMM 2114-568, Evaluation of Soft Goods From Thor Engine S/N 4090, 19 April 1962.

CEM 2114-505, Final Report of "42 Month" Thor Engine Soft Goods Evaluation Program," 15 January 1962.

CEM 2114-504, Evaluation of Soft Goods From Thor Engine S/N 4097, 15 January 1962.

CEM 1114-657, Evaluation of Soft Goods From Thor Engine S/N 4095, 7 September 1961.

CEM 1114-526, Evaluation of Soft Goods From Thor Engine S/N 4047, 6 March 1961.

CEM 1114-515, Soft Goods Analysis From Thor Engine S/N 4052, 26 January 1961.

CEM 0114-706, Analysis of Selected Soft Goods From G-26 Navaho Engine, 6 December 1960.

CEM 0114-686, Analysis of Soft Goods From Thor Engine S/N 4083, 1 November 1960.

CEM 0114-651, Analysis of Soft Goods From Jupiter Engines J3050, 3024, and 3054, 12 August 1960.

CEM 914-562, Investigation of O-rings From Redstone Engine Aging Program, 8 April 1959.

These reports describe programs conducted on soft goods from Rocketdyne engine systems. These programs have involved evaluations of various static and dynamic O-rings, seals, gaskets, diaphragms and assorted rings from selected engine teardown components. The basic analysis consists of a visual examination, and the determination of dimensions, hardness, and tensile strength. Tensile and compressive modulus tests, elongation, and compression set measurements have also been made on some of the O-rings.

It was concluded that the soft goods were in serviceable condition and were not adversely affected by the up to 46 months of rocket engine service. In addition to physical property tests on soft goods, a prime factor in determining the serviceability of the soft goods has been the actual functional testing of components. If the component functions properly, it is assumed that all parts have performed their designed function and it can be safely assumed that they have not deteriorated.

Roth, F. L. and R. D. Stiehler: "Strain Test for Evaluation of Rubber Compounds," Journal of Research of National Bureau of Standards, August 1948, 41-87.

This study uses tensile creep tests rather than tensile modulus tests for testing rubber materials in order to reduce errors introduced by having to measure load at a specified elongation. The decrease in elongation with time of cure is shown to follow a second-order reaction rate curve.

"Weather Aging of Elastomers on Military Vehicles," Rubber Age, July 1959.

This is a short aritcle about brief tests on ozone resistance of synthetic rubber (particularly SBR). Conclusions are that antiozonants should be added to rubber compounds. This is part of the "Effects of Ozone on Rubber" series in Rubber Age.

Scanlon, J. and W. Watson: "Interpretation of Stress Relaxation Measurements Made on Rubber During Aging," Transactions of the Faraday Society, 1958.

Scherer, L. T., Jr. and C. N. Blake: "The Determination of the Ultra Low Temperature Merit of Certain Silicone Elastomers by Means of the Temperature-Retraction Test," Technical Memorandum MT-M59, AD-291125, Chrysler Corporation Missile Division, 15 July 1958.

Specific information concerning the low-temperature performance limits of three types of silicone elastomers is presented. The authors used the temperature-retraction test because it permitted a rapid evaluation of crystallization effects and a spontaneous comparison of viscoelastic properties of rubber-like materials. This report does not present any detailed discussion of low-temperature phenomena. It concentrates on presenting temperature-retraction data on DC 916, DC 675 and DC 651 material.

Schafer, T. H.: "Preliminary Study of O-Ring Life," Convair Report No. ZX-8-006, EDEP Report No. 345.90.25.75-D6-01, 10 July 1957.

The life of O-ring seals under different experimental conditions was measured. "O-ring life" as used in this report means operating time to leakage of 0.005 cu in./min, when the system is operation under required temperature and pressure.

Fifty-four measurements of O-ring life were made under different test conditions exploring the influence of seven variables: surface finish (S), squeeze (Q), clearance (C), lubrication (L), rubbing speed, i.e., cycling frequency (R), rate of pressure variation (M), and temperature (T).

This is a very informative study discussing many of the parameters important to O-ring functioning, and many of the problems involved.

Shaw, R. F. et al: "Non-Destructive Aging Tests for Rubber," Analytical Chemistry, Vol 23, November 1951, 16-19.

This study describes the development of a strain tester for evaluating the effects of aging. Test specimens are subjected to definite loads or extensions at repeated intervals during exposure to the deteriorating influence of heat, light, air, and ozone. The degree of deterioration is evidenced by an elongation increase for specimens that become cracked and for a decrease in elongation for those that become heat-hardened.

Shelton, J. R.: "Effect of Temperature Upon Rate of Oxidation of Rubber, Nature of Resultant Deterioration," Industrial and Engineering Chemistry, Vol. 45, September 1953, 2080-2086.

Shelton, J. R., W. T. Wickham, and E. T. McDonel: A Study of Some of the Factors Involved in the Deterioration of Rubber Polymers and Vulcanizates, Status Report No. 1 to U.S. Army Office of Ordnance Research, 1 March 1955 to 31 May 1955, AD 86042, Case Institute of Technology, 1955.

This is a short progress report on work at the institute under a contract to study:

1. Oxidizability of polymers
2. Effect of mercury vapor on the rate of oxidation
3. Effect of milling on rubber aging
4. Studies on factors involved in the early stages of aging
5. Study of the mechanism of antioxidant action

Shelton, J. R. and W. T. Wickham: "Research on Oxidation and Aging of Natural and Synthetic Rubber," Case Institute of Technology, for Office of Ordnance Research, Final Report, Case Institute of Technology, 19 February 1955.

This research project is concerned with a study of the oxidation and aging behavior of natural and synthetic rubber polymers and vulcanizates. The present contract was particularly aimed at clarification and determination of:

1. The mechanism of the reaction of oxygen with rubber polymers and vulcanizates
2. The mechanism of antioxidant action in rubber polymers and vulcanizates
3. Optimum antioxidant concentrations and synergism
4. The extent to which various factors in the preparation and storage of specimens, as well as compounding variations, effect the initial stage of oxygen absorption
5. Such other factors as may develop pertinent to the objective

This study reports that while oxygen-absorption data usually make it possible to select the best prospects in a comparative study of antioxidants, it is also important to measure changes in physical properties. In most cases, the change in properties is in proportion to the oxygen absorbed, but there are some exceptions in which the degradation reactions are altered without a corresponding change in over-all rate of oxidation.

The question of the relative importance of thermal and oxidative effects was reinvestigated by comparison of the aging of a GR-S black stock in air, oxygen, and nitrogen. Significant differences were observed in aged properties obtained in the presence and absence of oxygen. The results indicate that thermal and oxidative effects are both important and that both should be included in a realistic study of the factors involved in the deterioration of rubber vulcanizates.

Shelton, J. R.: "Aging and Oxidation of Elastomers," Rubber Chemistry and Technology, Vol. 30, 1957, 1251-1290.

Smith, J. F.: "Aging: Its Cause and Prevention," Proceedings of the Institution of the Rubber Industry. Vol. 41, 1957, 138-142.

Soden, A. L., et al.: "Deterioration of Rubber Under the Influence of Light and Dry and Moist Heat," Transactions of the Institution of the Rubber Industry, Vol. 27, 1951, 223-231; also Rubber Chemistry and Technology, Vol. 25, 1952, 167-175.

Stickney, P. B. and L. E. Cheyney: "Plasticizers for Rubbers and Resins," Journal of Polymer Science, Vol. 3, 1948, 231-245.

This study provides excellent background for understanding of plasticizer action. The mechanism of plasticizer action has been discussed for linear, slightly and highly cross-linked polymers. The important factors considered are the flexibility of the polymer chain, the polar interaction of groups along the chain, the masking of these interactions by plasticizer molecules, and the importance of the relative shape of polymer unit and plasticizer in the effectiveness of separating the chains. For nonpolar polymers, without secondary valence cross links, the plasticization is largely an entropy effect since no secondary valence bonds are broken or formed.

Stickney, P. B. and W. J. Mueller: "Effect of Cure on Low-Temperature and Aging Properties of Nitrile Rubber," Rubber World, Vol. 134, May 1956, 334-338.

The object of this investigation was to establish the relative effectiveness of various levels of the vulcanizing agents in a conventional sulfur-accelerator curing system and a thiuram-disulfide type of curing system on the relation among heat and oil resistance, and low-temperature serviceability of nitrile rubbers.

This is an interesting laboratory study of some significance to the O-ring manufacturer, not to the end user.

Throdahl, M. C.: "Aging of Elastomers (Comparison of Creep With Some Conventional Aging Methods),) I and E C, Vol. 40, November 1948, 2180-2184.

It appears that the chemical reactions in elastomers at elevated temperature caused by oxidation, and which result in cross-linking and chain scission, are fundamentally exhibited by creep and stress relaxation. These interrelated functions have been used in this paper as a convenient means of studying the behavior of antioxidants and accelerators in Hevea and GR-S rubber. Tests conducted on several representative Hevea rubber stocks containing different pigments show that creep differentiates more clearly between antioxidants than do conventional aging tests. Creep measurements show that the relationships between the effectiveness of various antioxidants are independent of both accelerator and state of cure. Creep tests are shown also which differentiate GR-S tread stocks containing various antioxidants, although conventional aging tests indicate them to be alike. The relationship of continuous creep behavior with continuous and intermittent stress relaxation is shown in a typical Hevea vulcanizate containing combinations of three antioxidants with three types of accelerators. By either method, rating of antioxidant is the same for all three accelerators.

Tipton, F. W. et al.: "Design Data for O-rings and Similar Elastic Seals," WADC TR 56-272, Part I, AD 110598, November 1956.

For discussion, see entry under Trepus.

Trepus, G. E., et al.: "Design Data for O-Rings and Similar Elastic Seals," WADC TR 56-272, June 1957, Boeing Aircraft Co., Part I, November 1956 (Authored by W. Tipton) to Part VI, May 1961.

This is a very comprehensive study performed under Air Force contract to determine design criteria for O-rings, backup rings, and other elastomeric seals. A survey of current literature concerning seals and seal materials was conducted with an emphasis placed on seals and seal material for use in environmental extremes. The effects of environment and groove configurations on the sealing force of the O-ring were determined. Functional tests included pneumatic seal tests at 400 F, hydraulic rod seal tests at 400 F using O-rings and backup rings made from a variety of materials and in several configurations, static annulus and seal tests using various groove configurations. A preliminary aging study was also conducted.

van Raamsdonk, G. W.: "The Significance of Accelerated Aging Tests," Rubber Journal, November 1955.

This is a good discussion emphasizing the role of oxygen in aging, and the influence of the temperature of the aging test on the rate of oxidation. Unfortunately, it is mainly concerned with the effects of these parameters on natural rubber.

The author reports that the oxidation of natural rubber results in a chain scission of the molecules. It is predominantly the oxygen absorbed at the beginning of the process which causes a very pronounced reduction in the molecular weight of the rubber. The lower the temperature, the larger is the percentage of oxygen that can be combined without serious loss of tensile strength.

Accelerated aging should not be carried out at one temperature, as the temperature coefficient depends on the composition. For different compounds it could be proved that the log of the time necessary to reduce the tensile strength with 25% is a linear function of 1/temperature.

"First Progress Report - Investigation of Hydraulic Equipment Removed from B-24-D 'Lady Be Good' Aircraft," Vickers Incorporated, 7 July 1960; also "Evaluation Report - B-24-D 'Lady Be Good' Hydraulic Components," WWFESM-60-21, Wright Air Development Division, 29 March 1961.

A study was conducted on the hydraulic equipment removed from a 17-year old aircraft found on the Libyan Desert. Generally, the equipment was in good condition. The O-rings were tested and found to be in excellent condition.

Walker, W. R.: "Design Handbook for O-rings and Similar Elastic Seals," WADC TR 59-428, Boeing Aircraft Co., March 1961.

This handbook covers work performed by Trepus et al on the mechanism of O-ring sealing.

Data are presented concerned with hydraulic and pneumatic systems utilizing static and dynamic-type seals at temperatures exceeding 275 F and for static applications at cryogenic temperatures. The effect of vibration, pressure cycling, seal materials and fluids on the operational efficiency of seals and backup rings are discussed. Sections are devoted to cryogenic, fuel, and vacuum system seals, and aging and age control. It also includes physical properties of elastomers at high temperatures and a bibliography.

This is a very important and significant contribution to the field in providing guidelines to designers for sealing system evaluation and a basis for proper material selection.

Webber, A. C.: "Brittleness Temperature Testing of Elastomers and Plastics," American Society for Testing Materials (ASTM) Bulletin, July 1958, 62-64.

Youmans, R. A. and C. G. Maassen: "Correlation of Room Temperature Shelf Aging With Accelerated Aging," Industrial and Engineering Chemistry, Vol. 47, July 1955, 1487-1490.

This is a good study in which the authors attempted to correlate actual room-temperature shelf aging of natural rubber with various accelerated aging tests. From the data reported, the following general statements can be made:

1. During natural storage, not all physical properties change at the same rate.
2. During accelerated aging not all properties change at the same relative rates as during natural aging.
3. None of the usual accelerated aging tests predicts accurately all of the physical changes that will take place on long-time storage.
4. Of the three accelerated heat aging tests, all will predict with some degree of accuracy the trend in breaking tensile and breaking elongation during limited long-time storage.
5. Of the three types, the air bomb is least reliable for predicting modulus change at normal temperatures. The 70 C oxygen bomb exposure is somewhat more reliable. The best method is the 70 C circulating air oven. For this particular stock, it could be used for predicting shelf life up to 6 years.

TASK 2--STUDY OF O-RINGS IN CRYOGENIC SYSTEMS

In previous Rocketdyne analyses of the soft goods from liquid rocket engine systems, several indications of the possible accelerated degradation of O-rings in LOX service have appeared. This degradation generally took the form of appreciably more severe checking or cracking of LOX system O-rings than that found in the remaining rings from the same engine system. Typical O-rings showing this effect were found in the LOX start tank during the analysis of Thor engine Serial No. 4291.

Rocketdyne has studied the behavior of O-rings in LOX service to determine if such rings are appreciably different in their relative rates of aging and degradation of properties (and therefore require distinct age control limits) from those used in fuel, hydraulic, and pneumatic service. Three distinct approaches have been taken in this study.

To evaluate the effect of low temperature alone,one series of tests has been run on O-rings exposed periodically to cryogenic temperatures in nonoxidizing environments.

A second approach to this study was to determine if accelerated elastomer degradation results from exposure to a 100% gaseous oxygen (GOX) atmosphere. This approach was prompted by the possibility of GOX phases existing after routine engine checkouts involving the loading of LOX. Virtually all investigators consider oxygen to be the prime cause of degraded, unsaturated-type elastomers (such as nitrile rubber).

A third approach to the over-all problem of O-rings in LOX environments is to determine the effect of thermal contraction on O-rings installed on a typical shaft. This provides an opportunity to investigate the effects of varying O-ring strains (at ambient temperature) on subsequent contraction behavior (at cryogenic-temperatures).

This section presents a discussion on each of these three series of tests. It includes a review of the test procedures used throughout these studies, as well as discussions of special tests employed to explain some of the phenomena observed.

TEST PROCEDURES

Hardness and W-Diameter

Shore-A hardness readings and W-diameter measurements were made on each O-ring in at least five points equally distributed around its circumference. A spring-actuated hardness instrument and a deadweight micrometer (0.0010-inch graduations) were used.

Tensile Properties (Tensile Stress, Ultimate Elongation, Tensile Strength)

The tensile tests were performed at ambient conditions on a calibrated Instron Universal Testing Machine at a crosshead speed of 20 in./min. The test were generally conducted in accordance with the ASTM method for tension testing of rubber O-rings (ASTM No. D1414-56T). This method utilizes jaws having 1/2-inch-diameter, automatically rotated spools over which the O-ring is stressed. The tensile stress (at 100% elongation), ultimate elongation, and tensile strength were determined on the same O-ring sample. The appropriate calculations are based upon the original cross-sectional area of the O-ring.

The elongation measurements were obtained by observing the distance between the gage length marks, which were initially 1/2 or 1 inch apart.

Compressive Properties (Compression Set, Compressive Stress, Compressive Relaxation)

Compression-set tests were performed in accordance with ASTM D395-61, Method B (Compression Set Under Constant Deflection), except that O-ring samples were used. The compression set is expressed as a percentage of the original deflection, and is calculated as follows:

$$C = \frac{t_o - t_f}{t_o - t_s} \times 100$$

where

C = compression set expressed as a percent of original deflection (approximately 25 to 35%)

t_o = original W-diameter

t_f = W-diameter at room temperature after 70 hours at 212 F

T_s = thickness of spacer bar used

Compressive stress tests (compression-deflection) utilized an Instron Universal Testing Machine to compress the O-rings, between two parallel plates, up to 60% deflection (measured by a dial indicator). The rate of crosshead movement was 0.02 in./min.

The data reported are expressed as the compressive force (pounds) to compress the ring a fixed percent per inch of circumference (mean) of the O-ring.

Compressive relaxation tests were performed by compressing the O-rings to a fixed 20% deflection utilizing the Instron machine. The change in load over a predetermined time interval was recorded on the Instron strip recorder chart.

All of the testing was performed at room temperature (77 ±5 F).

Temperature Retraction Tests

The low-temperature retraction test has been performed per ASTM D1329-60 except that O-ring samples, cut to form a single strand, were used. The test is conducted by (1) elongating the sample, (2) locking it in the elongated condition, (3) freezing it to practically a nonelastic state, (4) releasing the frozen specimen and allowing it to retract freely while raising the temperature at a uniform rate, (5) reading the length of the specimen at regular temperature intervals while it is retracting, and (6) computing the percentage retraction values at these temperatures from the data obtained.

The apparatus used by Rocketdyne is shown in Fig. 1 . The O-rings, cut to form a single strand, were initially elongated to 50% and then frozen in a dry ice-methanol mixture (-150 F). The heating coils were adjusted to raise the temperature 1.8 F per minute.

THE EFFECT ON O-RINGS OF PERIODIC EXPOSURE TO CRYOGENIC TEMPERATURE (-320 F)

Selection of Test Conditions and Samples

To explore the effects on LOX system O-rings of exposure to cryogenic temperatures, it was decided to attempt to simulate actual conditions as closely as possible, within the scope of this program.

It was decided to use liquid nitrogen (-320 F) as the cryogenic environment rather than the more reactive liquid oxygen (-297 F) to separate the effects of low temperature from oxidation effects, and to facilitate the testing program.

After consultation with Rocketdyne engine systems engineers, as well as with the contracting agency, it was decided that 300 minutes represents a realistic time for exposure of LOX system rings to cryogenic temperatures. Therefore, the cycling tests were arranged so as to duplicate this exposure period.

Because only MIL-G-5510A (MS28778) rings are used as static seals in LOX systems, only these rings were used in this study. All tests were

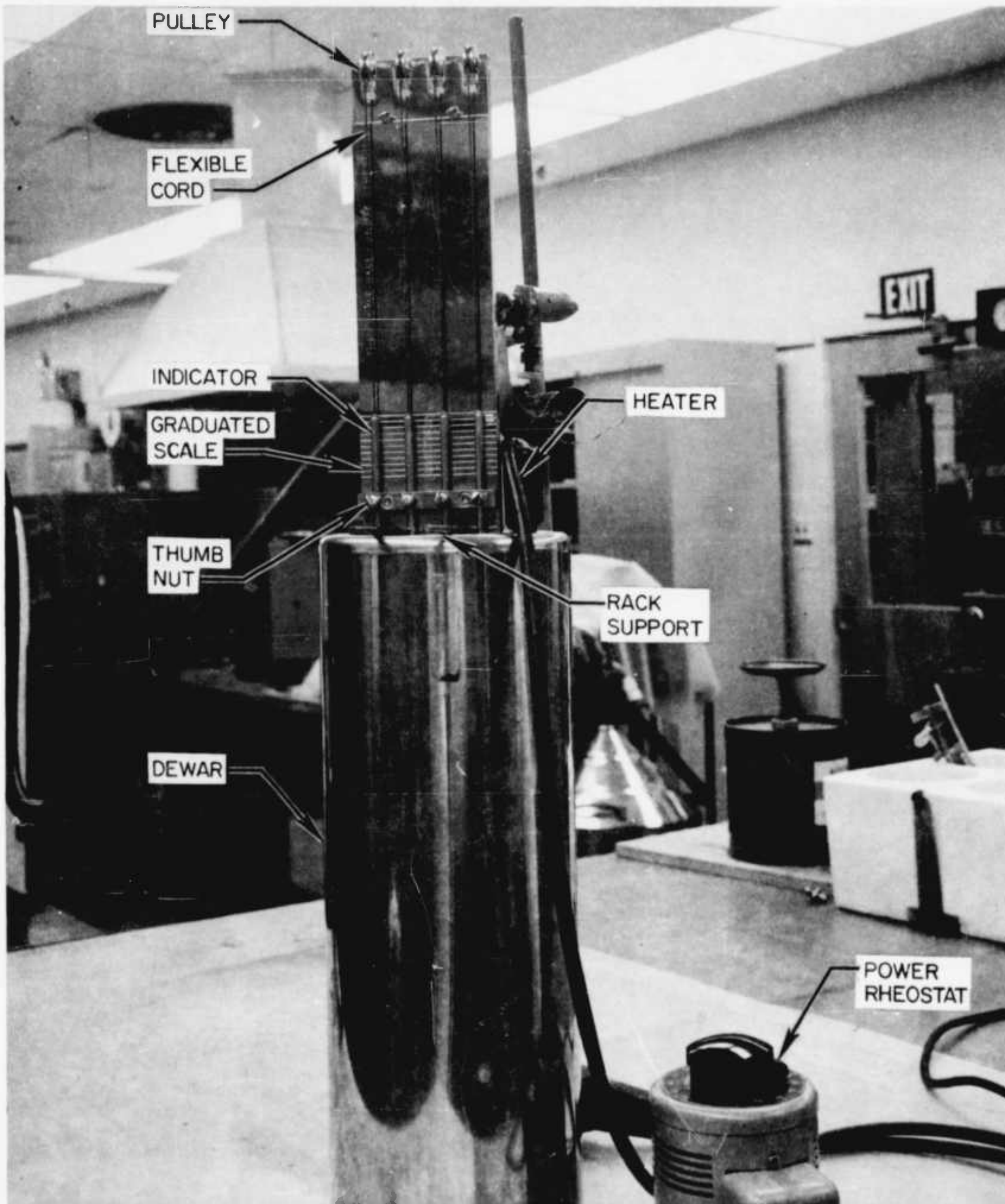


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Figure 1. Low-Temperature Retraction Apparatus

conducted on either MS28778-8 or -16 rings obtained from the Parker Seal Company. The following dimensions and tolerances are specified in the MS drawing for the rings:

	MS28778-8	MS28778-16
"W" Diameter	0.087 ±0.003	0.166 ±0.004
Inside Diameter	0.644 ±0.005	1.171 ±0.006

Property Testing

Preliminary Test Phase. In the preliminary test phase, both stressed and unstressed MS28778-8 and -16 rings were cycled 10 times between ambient temperature (approximately 77 F) and -320 F. A cycle consisted of a 30-minute immersion in liquid nitrogen, followed by a 45-minute "rest" period at ambient temperature. The stressed rings were circumferentially stretched approximately 15% on a stainless-steel shaft.

Physical property tests (tensile and compressive series) were performed at room temperature approximately 12 to 15 hours after the completion of the 10 cycles, then compared with values determined on control rings from the shelf. The data are summarized in Tables 6 through 8 and represent average values. Appendixes A and B present the actual data.

It was seen consistently that cryogenic cycling had the greatest effect on stretched O-rings. For the MS28778-16 rings, the ultimate tensile strengths for the stretched rings increased to an average of 1600 psi from a control value of 1483 psi. O-rings cycled in an unstretched condition were found to have a tensile strength of 1509 psi. In a similar

TABLE 6

SUMMARY OF TENSILE DATA FOR CRYOGENIC EXPOSURE STUDY (10 CYCLES)

O-Ring Type	Condition Imposed	Average Tensile Strength, psi	Average Elongation, %	Shore-A Hardness
MS28778-16	Control	1483	110	80
MS28778-16	Unstressed	1509	106	80
MS28778-16	15% Stretch	1600	105	82
MS28778-8	Control	1659	104	80
MS28778-8	Unstressed	1507	104	80
MS28778-8	15% Stretch	1650	97	82

TABLE 7

SUMMARY OF COMPRESSIVE LOAD DEFLECTION DATA FOR CRYOGENIC EXPOSURE STUDY (10 CYCLES)

O-Ring Type	Deflection, %					
	10	20	30	40	50	60
MS28778-16 Loads, pounds						
Controls	79	168	305	556	1057	2240
Unstressed	72	156	287	520	993	2100
15% Stretch	50	125	238	440	809	1620
MS28778-8 Loads, pounds						
Controls	35	76	137	245	480	1140
Unstressed	30	67	124	225	438	1014
15% Stretch	26	62	118	218	430	978

TABLE 8

SUMMARY OF COMPRESSION-SET DATA FOR CRYOGENIC EXPOSURE STUDY (10 CYCLES)

O-Ring Type	Condition Imposed	Deflection, %	Compression Set, %
MS28778-16	Control	35	41
MS28778-16	Unstressed	35	33
MS28778-16	15% Stretch	34	29
MS28778-8	Control	36	45
MS28778-8	Unstressed	37	32
MS28778-8	15% Stretch	34	27

manner, a corresponding decrease in compressive load (Fig. 2) and compression-set values were noted after the O-rings were cycled. In all cases, only a marginal increase in hardness values was noted.

With the smaller MS28778-8 rings and unstressed condition, the changes in property values were not as great as for the MS28778-16 rings and stressed conditions, but were still noticeable. Therefore, in subsequent studies, only MS28778-16 rings in stressed conditions were used.

Sensitivity of Properties to Number of Cryogenic Exposures. To determine if changes in mechanical properties are sensitive to the number of cryogenic exposures, a comparison was made between the properties of MS28778-16 rings after 10 cycles (30 minutes liquid nitrogen exposure per cycle) and after 20 cycles (15 minutes liquid nitrogen exposure per cycle) of exposure to liquid nitrogen. The total exposure time (300 minutes) is the same in both situations. These data are reported in Table 9 and Appendix A.

For both the unstressed and the stressed O-rings, the tensile strength increased from 1510 and 1600 psi at 10 cycles to 1720 and 1830 psi and 20 cycles. A decrease in elongation also was observed from 106 and 105% at 10 cycles to 96 and 96% at 20 cycles. A marginal increase was noted in hardness measurements, but no significant difference could be detected in compression set (at 25% deflection for 70 hours at 212 F) or compression-deflection characteristics.

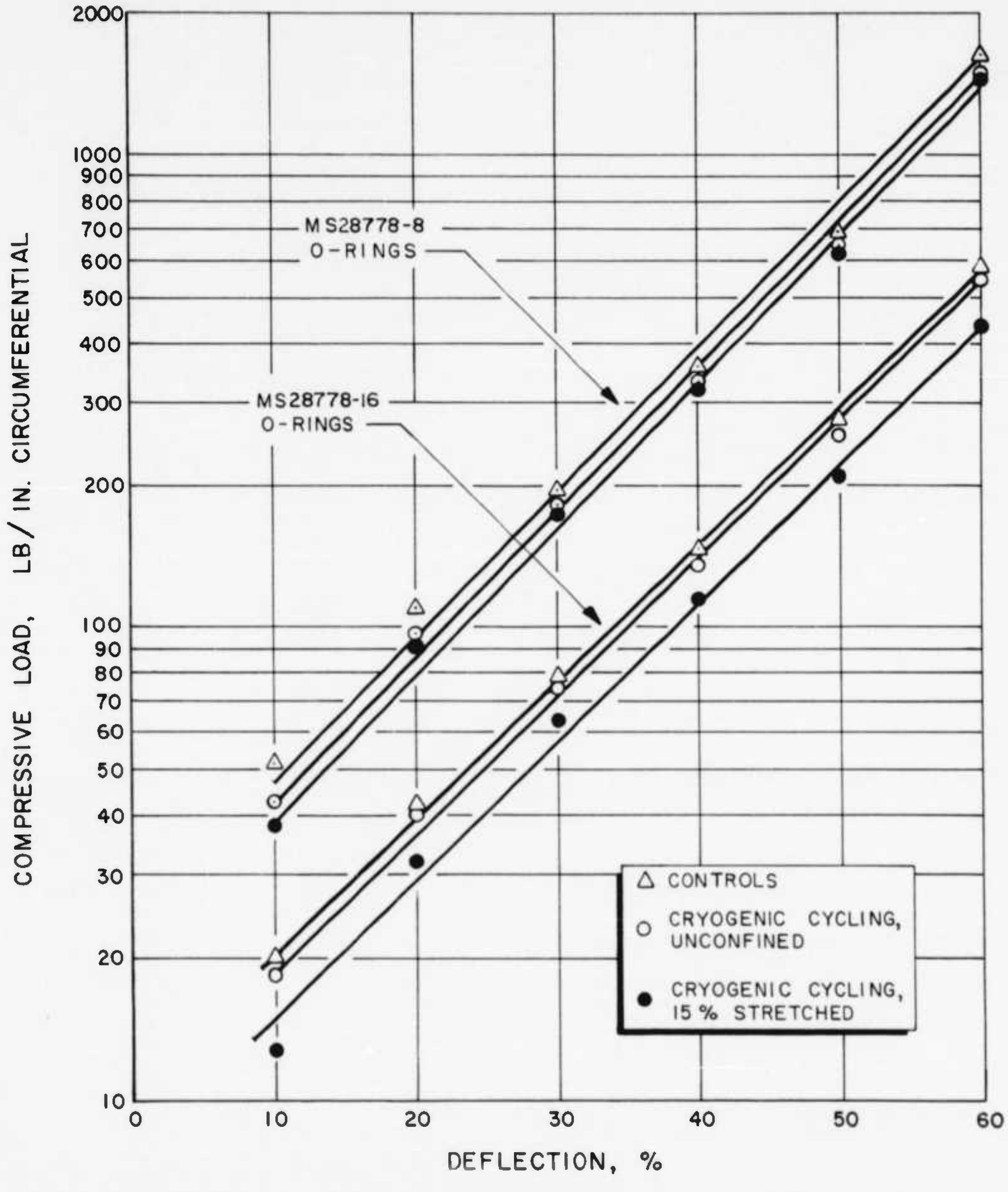


Figure 2. Compressive Load vs Deflection Curves (Cryogenic Exposure Study)

TABLE 9

EFFECT OF NUMBER OF CRYOGENIC CYCLES ON TENSILE STRENGTH AND ELONGATION OF MS28778-16 O-RINGS

Number of Cycles	Condition	Tensile Strength, psi	Elongation, %
0	Controls	1483	110
10	Unstressed	1509	106
	15% Stretch	1600	105
20	Unstressed	1720	95
	15% Stretch	1830	95

Compressive Stress Relaxation Study

As will be discussed in the Task 3 section of this report, the compressive stress relaxation property is closely related to the O-ring sealing mechanism. Thus, to explore further the effect of cyrogenic cycling on O-rings, stress relaxation studies at 20% compressive deflection were made on 20-cycle, liquid nitrogen-exposed, new MS28778-16 O-rings, and also on an in-service MS28778-16 O-ring having the following history:

1. Removed from LOX integrated start tank
2. Engine type: XLR79-NA-9
3. Engine serial number: NA004280
4. Date removed: 28 August 1962
5. Service life: 39 months
6. LOX flow exposures: 11

The 20-cycle exposure was used because it has a greater effect on the O-ring than does the 10-cycle exposure. The load decay was measured immediately after cycling and after a 1-week recovery period to determine if varying recovery periods affect the stress relaxation results. Data from this study appear in Table 10 and Appendix C, and represent stress decay values measured after the compressive load had been applied to the ring for 15 minutes. Figure 3 illustrates the stress relaxation behavior of the test rings.

In a series of calibration runs, it was found that 66% of the total stress decay occurs after 15 minutes. After 3 additional hours, the stress decay levels out to a constant value (Fig. 4). Thereafter, to save time, load decay was determined after 15 minutes.

TABLE 10

SUMMARY OF COMPRESSION RELAXATION DATA OF MS28778-16 O-RINGS (20% COMPRESSION)

Condition Imposed	Initial Load, pounds	Immediate Load Drop, pounds	Immediate Load Loss, %	Final Load After 15 Minutes, pounds	Total Drop After 15 Minutes, %
Control	152	138	9.0	106	30.2
Unstressed:					
Tested Immediately	145	134	7.7	106	27.2
Tested After 5 Days	148	137	7.7	107	27.5
15% Stretch	137	126	7.9	99	27.6

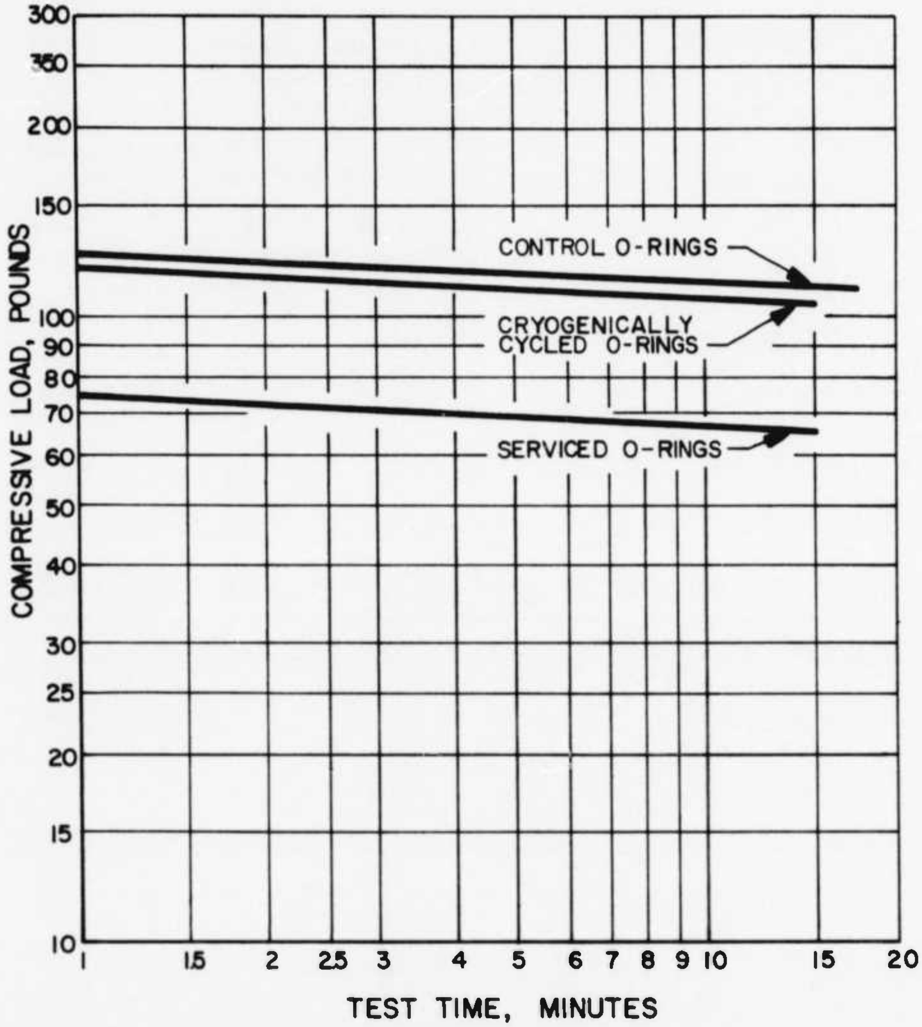


Figure 3. Stress Relaxation Behavior of Cryogenic-Cycled O-Rings

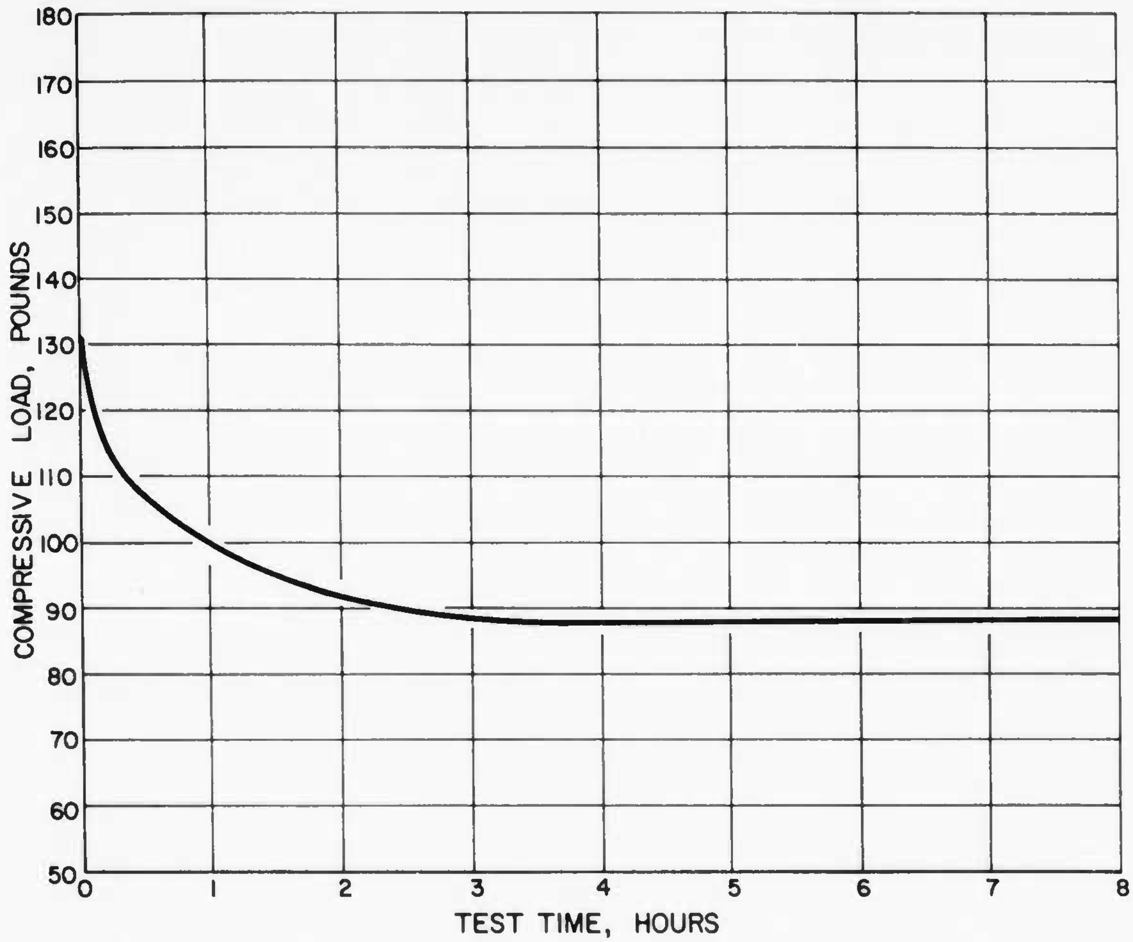


Figure 4 . Stress Decay Curve (Calibration Run)

Small, but detectable differences appear in the stress relaxation values of uncycled controls and cycled O-rings. The percent drop in compressive load after 15 minutes is approximately 30% for controls, compared to 27% for the 20-cycled rings. No detectable differences were found between the unstressed and stressed cryogenically cycled rings or between rings which were allowed to recover for periods varying from 0 hours to 1 week.

Low-Temperature Retraction Tests

In determining low-temperature serviceability, retraction tests are frequently used as an indicator of the flexibility of an elastomer during and after exposure to low temperatures. In addition to the physical properties evaluations of O-rings after exposure to cryogenic temperatures, low-temperature retraction tests were conducted.

As the temperature is lowered, elastomeric compositions stiffen progressively until the brittle point of the material is reached. This decrease in flexibility is caused by the increased internal viscosity of the molecular chains (as the temperature decreases). The brittle point is the temperature at which the material hardens, becomes brittle, and shatters upon the sudden application of load. Although an additional decrease in flexibility may be caused by an increase in the crystallinity of the polymer, this effect is not believed to be appreciable in copolymer systems, such as nitrile rubber, which are most frequently used in AN and MS O-rings.

The procedures for conducting low-temperature retraction tests are discussed on pages 76 through 83 . In reporting the data temperatrue retraction (TR), the temperatures corresponding to 10 and 70% retraction are of particular importance, and are designated as TR 10 and TR 70, respectively. Usually, TR 10 measurements are influenced by viscoelastic effects, and have some correlation with the brittle points of elastomers. TR 70 values have been found to be influenced by crystallization effects and with low-temperature compression set.

Figure 5 illustrates typical retraction curves for natural rubber, nitrile rubber, and neoprene (Ref. 12). The slopes of the curves are indicative of crystallization capabilities and indicate that nitrile rubbers are considerably less subject to crystallization than either natural or neoprene rubber.

Because the rubber will remain stiff and rigid from liquid nitrogen temperatures up to the brittle point, there is no reason to conduct retraction tests at temperatures within this range. Therefore, tests were begun and retraction values obtained at a temperature sufficiently low to freeze the rubber. MS28778-16 size rings, cut to form a single strand, were used throughout the study.

In Fig. 6 , temperature retraction curves of control O-rings are compared to temperature retraction curves of O-rings that had undergone 20 cryogenic cycles (15-minute duration) in liquid nitrogen while subjected to 15% circumferential stress. Also shown are curves from O-rings that were immersed in liquid nitrogen for a single 15-minute period while subjected to 50% circumferential stress.

A temperature retraction curve is also presented for an "in-service" MS28778-16 O-ring which has the following history:

1. Removed from LOX integrated start tank

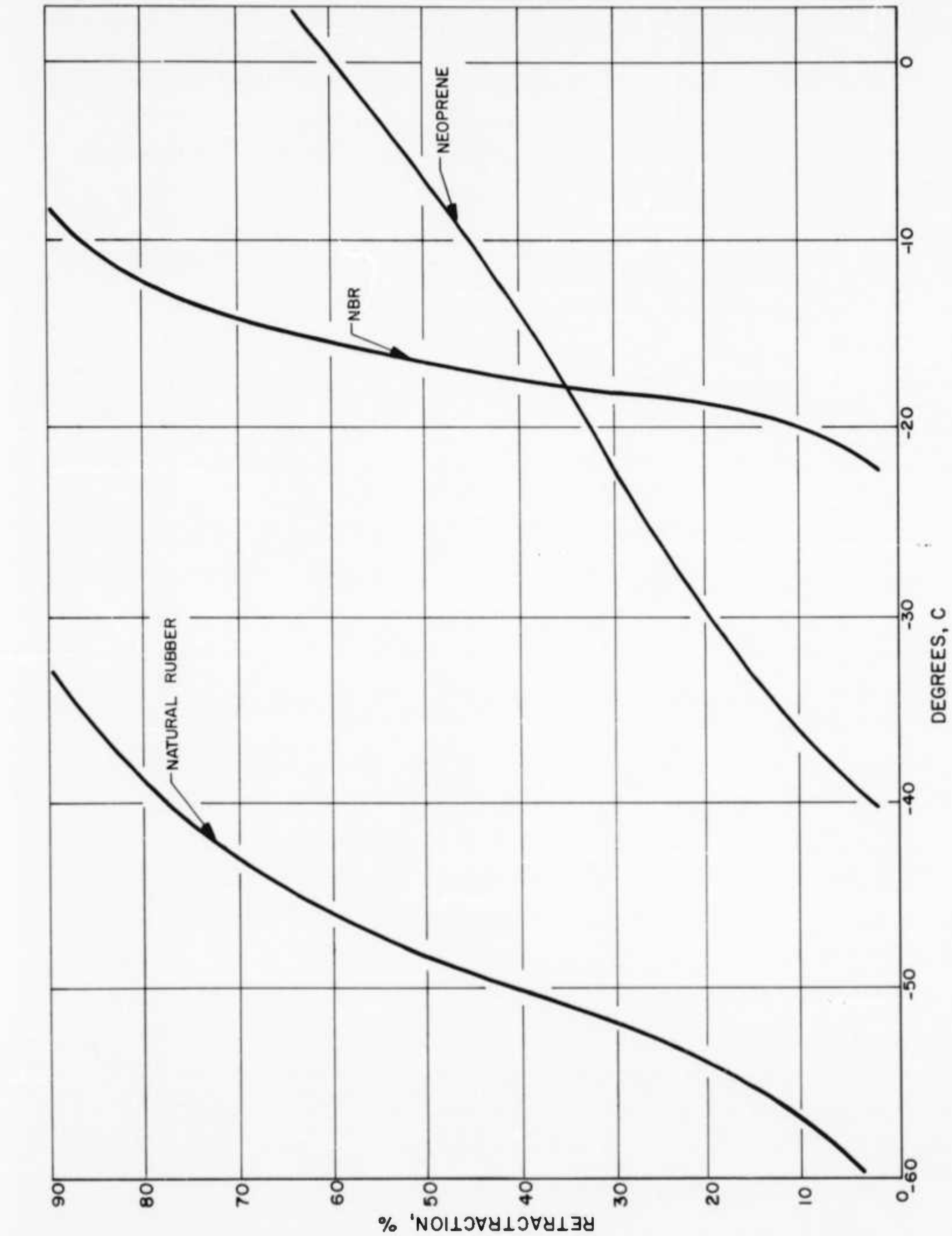


Figure 5. TR-50 Curves for Representative Elastomers
(Conditioned 1 hour at 70 C)

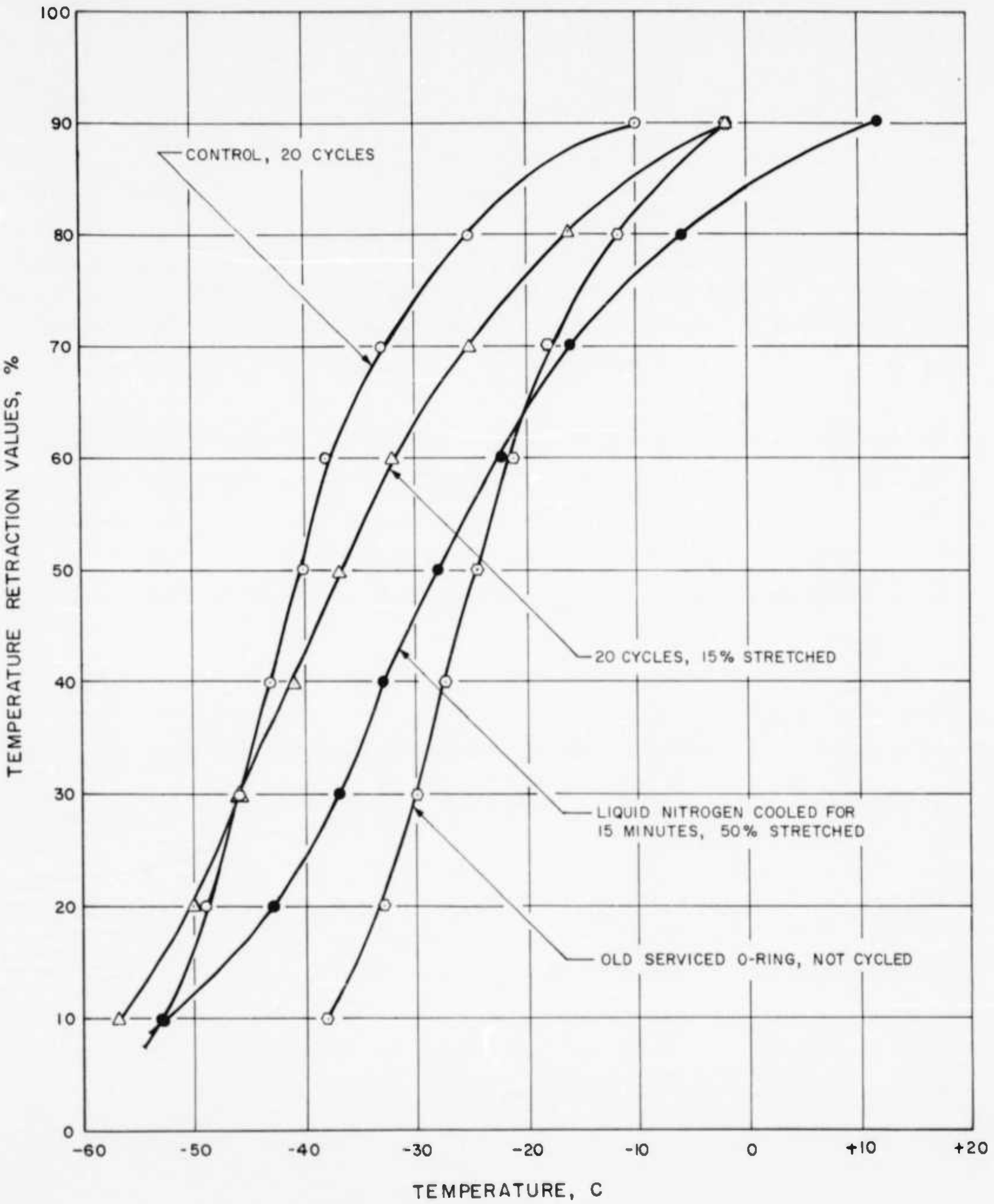


Figure 6. Low-Temperature Retraction Curve For Cryogenic-Cycled and Control O-Rings

2. Engine type. XLR79-NA-9

3. Engine serial number: NA004291

4. LOX flow exposure - 16

The observation that the test rings are displaced to the right of the control temperature retraction curve indicates an additional stiffening of these rings and a greater internal viscosity.

Further testing was performed on two specially formulated vulcanizates from Parker Seal Company (similar to MS28778), one of which was formulated with plasticizer, while the other was formulated without plasticizer. The temperature retraction curves shown in Fig. 7 indicate an appreciable difference between the retraction behavior of plasticized and unplasticized compounds. For example, the TR 10 value is much higher for the unplasticized O-ring (-38 C compared to -49 C). Both compounds, however, exhibited an additional stiffness when stretched at cryogenic temperatures. The largest deviation occurred when the rings were 50% stretched and cooled in liquid nitrogen for 15 minutes.

<u>Plasticizer Effects Study</u>

The unanticipated findings of increased hardness and tensile strength decreased elongation; generally, a decreased resiliency of the rings at room temperature, after cryogenic cycling, has prompted speculation as to the reason for such occurrences.

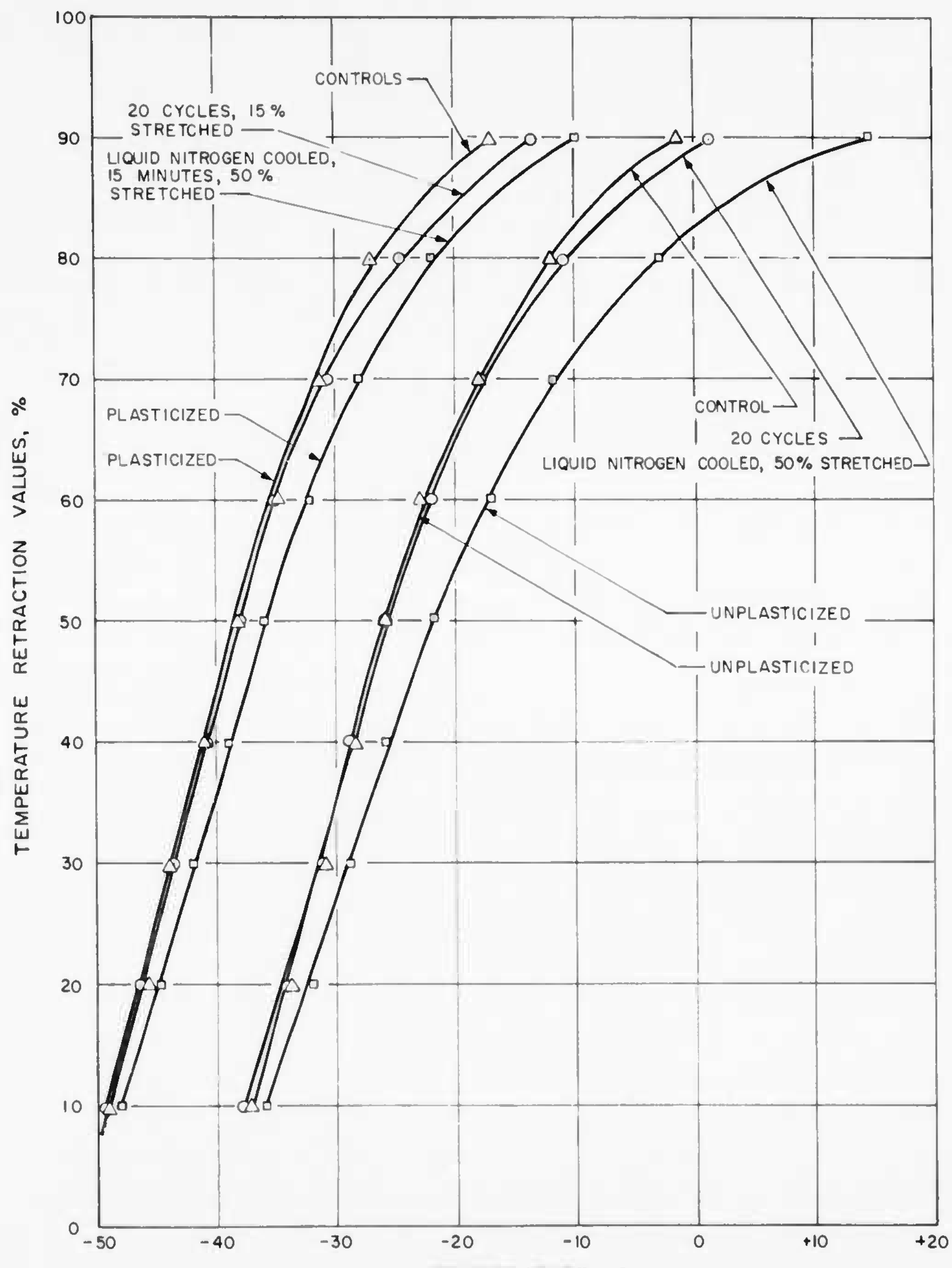


Figure 7. Low-Temperature Retraction Curves of Plasticized and Unplasticized Compounds

Because these particular rings are generally highly plasticized to impart good low-temperature flexibility (to meet military specification requirements of flexibility down to -65 F) and because a loss of plasticizer generally results in a harder ring, it seemed logical to investigate the situation from a plasticizer-loss viewpoint.

The hypothesis that the anomalous behavior of the MS28778 0-rings after cryogenic cycling is attributed to loss of plasticizer or to loss of plasticizing action has been investigated by:

1. Performing Soxhlet extractions with toluene on both cryogenic-cycled and new 0-rings
2. Determining the weight change, if any, or rings exposed to cryogenic temperature cycling
3. Testing two variations of a specially formulated compound (basically an MS28778 compound), one plasticized and the other unplasticized

Soxhlet Extractions on 0-rings. To determine if any placticizer was extracted during the cryogenic-temperature cycling of MS28778-16 rings, Soxhlet extractions with toluene were carried out on both cycled and new 0-rings. Lower extraction values (compared to new 0-ring controls) of the cycled rings would be indicative of a loss of plasticizer during the cycling process.

The percent extractables in both 0-rings were determined by refluxing with toluene for 24 hours; in these tests, the 0-ring samples were cut into small places and kept in porous thimbles (Soxhlet extractors).

After the refluxing was completed, the swollen samples were dried at 100 C until constant weights were obtained. The percent solubles in toluene then was calculated from the initial and final weights of a vulcanizate.

Weight Changes. It may be seen from the data in Table 11 that no substantial difference in O-ring weight loss was detected by the Soxhlet method, which would lead one to suspect that plasticizer was extracted. Furthermore, any differences in O-ring weights before and after cryogenic cycling were negligible. However, plasticizer migration to the surface of the O-ring vulcanizate, and its subsequent removal by mechanical means, is probably a gradual process and cannot be detected at once. Although the incompatibility or insolubility of plasticizer in the elastomer probably occurs immediately after the cycling process, it requires a certain time element for its actual removal from the elastomer lattice. This speculation was prompted by the observation of an oil-like staining of the paper toweling in which the cycled O-rings were kept wrapped for approximately 6 months.

Specially Formulated Compounds. Initial work to determine physical properties on a limited number of plasticized and unplasticized O-rings of the MS28778-16 type was started to determine the effect of cryogenic temperatures on a plasticized material.

Two specially formulated compounds were prepared for Rocketdyne by the Parker Seal Company. Both compounds are composed of the same ingredients that are used in Parker's Military Specification MS28778 rings (Parker Compound No. 145-140). However, to have a reasonably moldable compound

TABLE 11

SOXHLET EXTRACTION TESTS ON O-RINGS

Parameter	Sample No. 1	Sample No. 2
Cycled O-Rings		
Initial Weight, grams	0.3960	0.4119
Final Weight, grams	0.3542	0.3710
Weight Loss, %	10.55	9.93
Control O-Rings		
Initial Weight, grams	0.3994	0.4106
Final Weight, grams	0.3573	0.3665
Weight Loss, %	10.54	10.74

when the plasticizer is removed, it was necessary initially, to reduce the carbon black content. Both special compounds are identical except for plasticizer content. Compound XN 1340-1 contains no plasticizer. Compound XN 1340-2 contains 7.692% (by weight) of an ester-type plasticizer (an adipate).

Physical property tests, similar to those run on the MS28778-8 and -16 rings, were performed on the two specially formulated rings. These results are reported in Table 12 and Appendix D.

As anticipated, the controls indicated that the unplasticized rings were harder and stiffer than the plasticized rings. However, it is interesting to note that, although the elongation values remained essentially the same after 20 cryogenic cycles for the unplasticized rings, the values for the plasticized rings decreased appreciably.

Also, the low-temperature retraction tests (discussed on pages 76 through 83) indicate that there is a decreased flexibility of the plasticized O-ring after cryogenic exposure when compared to the unplasticized rings.

These observations on changed properties of plasticized rings caused by exposure to cryogenic temperatures, coupled with reports in the literature, provide some verification for the hypothesis that plasticizer effects--whether it be plasticizer incompatibility, plasticizer migration, or a combination of the two is not known--are responsible for the change in O-rings after cryogenic exposure. Certainly, more conclusive data are necessary. This area should be explored in future studies.

TABLE 12

SUMMARY OF TENSILE AND ELONGATION DATA FOR SPECIAL PLASTICIZED AND UNPLASTICIZED O-RINGS (20 CRYOGENIC EXPOSURES)

O-Ring	Condition	Tensile Strength, psi	50% Tensile Stress, psi	Elongation, %
Plasticized	Control	2010	328	169
Unplasticized	Control	1830	558	122
Plasticized	15% Stretch, 20 Cryogenic Cycles	1735	458	136
Unplasticized	15% Stretch, 20 Cryogenic Cycles	2087	725	121

X-Ray Diffraction Study

To determine if the permanent stiffening of O-rings during cryogenic exposure is the result of effects other than those associated with plasticizers, X-ray diffraction studies were employed.

Natural rubber and certain synthetic elastomers are known to exhibit a crystallinity buildup at low temperatures (Ref. 13). Such a phenomenon would result in a harder material having a lower ultimate elongation, an increased tensile strength and, generally, a lower resilient material, all of which were encountered.

Nitrile rubber is not reported to be crystallizable (Ref.13), i.e., it does not develop increased crystallinity upon exposure to low temperature. This is in accordance with theories in which it is considered that any increase in the degree of crystallinity is synonymous with increased order and regularity in the molecular chain. Such order is not readily possible with a material like nitrile rubber, which is a copolymer chemically composed of two distinctly structurally-different constituents--acrylonitrile and butadiene. Because very limitied work has been reported on crystallinity effects on nitrile rubber after exposure to cryogenic temperatures, it was considered worthwhile to explore the possibility of such crystallinity development after the cryogenic cycling exposures.

The X-ray diffraction study utilized a General Electric XRD-5 X-ray diffraction unit. Copper potassium gamma (CuK_{γ}) radiation was employed. The samples were segments cut out of the O-ring.

X-ray diffraction patterns of unstressed O-rings (subjected to 20 cycles of liquid nitrogen exposure) and new O-rings were compared to determine if some unanticipated crystallinity buildup had occurred. No differences in the Debye-Scherrer X-ray patterns were detected (Fig. 8). This tends to confirm the suspicion that no crystallinity buildup occurred during the cryogenic cycling.

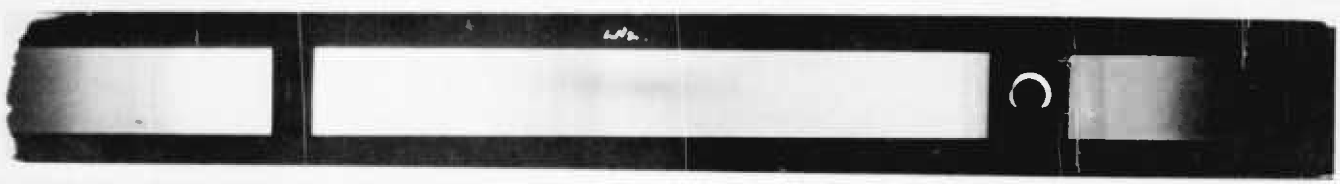
Weather Checking of Cryogenic-Cycled O-Rings

After cryogenic cycling, O-rings which were exposed to ambient atmospheric conditions in a stressed condition were found to exhibit severe ozone-like cracks perpendicular to the stress. Figure 9 is a photograph (magnified 5 times) showing the condition of MS28778-12 O-rings after 1 week ambient air-exposure in a 30% circumferentially stretched condition (on a stainless-steel shaft). The rings had undergone 7 cycles between room temperature and -320 F. The cycles consisted of 15 minutes in liquid nitrogen and 45 minutes at room temperature.

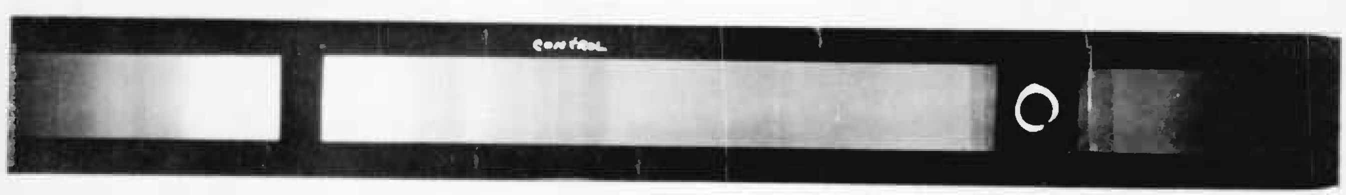
Although similar effects were found on control O-rings, the weather checking shown in Fig. 10 was less pronounced than in O-rings exposed to cryogenic temperature. Figure 10 illustrates the contrast in appearance between the control MS28778-12 O-rings (no cryogenic-cycling, but exposed to atmosphere for 1 week) and O-rings previously cycled four times between liquid nitrogen and room temperature (15 minutes in liquid nitrogen, 45 minutes at room temperature). The apparent influence of cryogenic cycling on weathering is not understood but, probably, exposure to the liquid nitrogen affects the chemical structural nature of the elastomer.

It should be pointed out that the checking was probably exaggerated because of the relatively high elongation used. Normal applications would not involve elongations over 10 to 15%.

CONDITION: UNSTRESSED, 20-CYCLE LIQUID NITROGEN EXPOSED

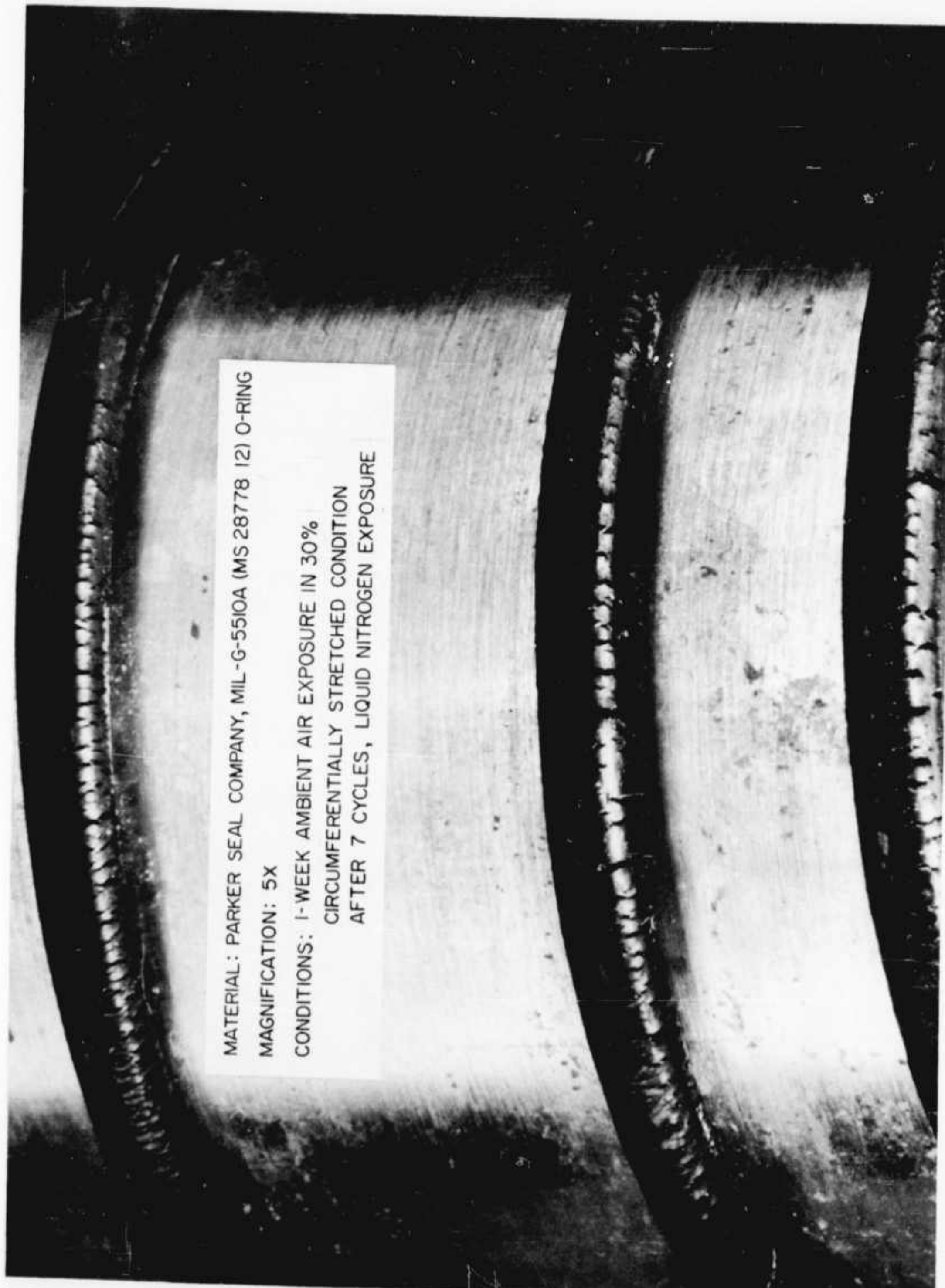


CONDITION: CONTROL, NEW RING, UNEXPOSED TO LIQUID NITROGEN



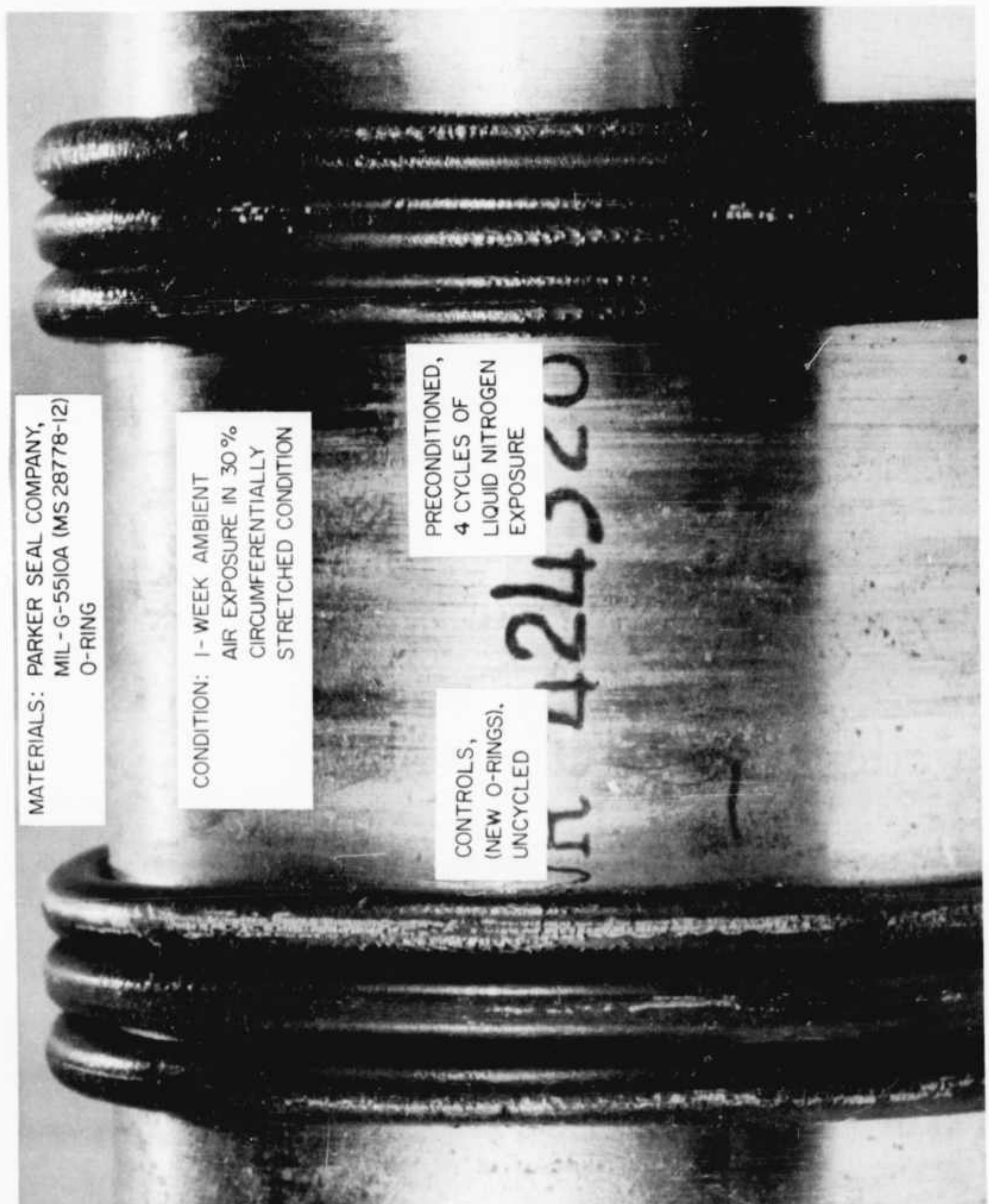
NOTE: MATERIAL IN BOTH CASES IS FROM
PARKER SEAL COMPANY, MIL-G-5510A (MS 28778)
BUNA-N O-RINGS.

Figure 8. Debye-Scherrer X-Ray Deffraction Patterns: Liquid Nitrogen-Exposed O-Ring vs Unexposed O-Ring



1BG65-5/7/63-C1

Figure 9. Weather Checking of Cryogenic Cycled O-Rings



1BE65-5/21/63-C2

Figure 10. Comparison of Weather Checking of Cryogenic-Cycled O-Rings with Uncycled O-Rings

100% GASEOUS OXYGEN ATMOSPHERE STUDY

Because oxygen is considered by virtually all investigators to be the prime cause of elastomer aging, and because there is a possibility of a gaseous oxygen atmosphere existing after routine engine checkouts involving LOX loadings, a study was performed to determine if accelerated elastomer degradation results from exposure to a 100% gaseous oxygen atmosphere.

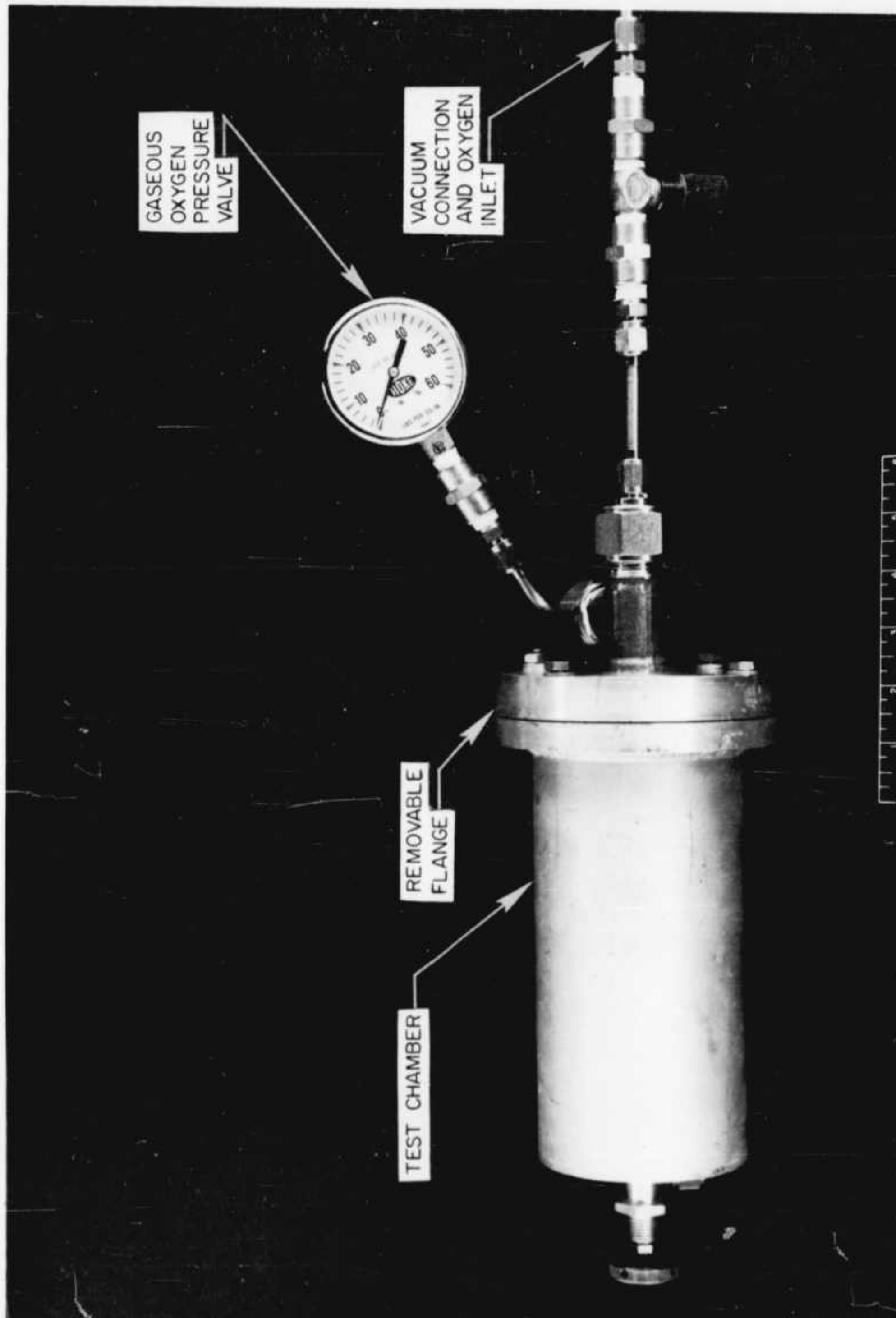
Test conditions were selected to provide a longer exposure period (10 days at ambient temperature) than the rings would have in service. A special oxygen exposure chamber (Fig. 11) was fabricated and used for this study. After the appropriate samples (stresses or unstressed) are loaded into the chamber, the chamber is evacuated, then pressurized with oxygen to 20 psig.

Physical property tests were conducted on both stressed and unstressed O-rings after they had been exposed for 10 days at ambient temperature. These results are included in Table 13 and Appendix E.

With no appreciable changes detected in tensile strength and compression-deflection characteristics, it appears that oxygen exposure for the 10-day period did not affect the elastomeric compounds under consideration.

THERMAL CONTRACTION EFFECTS ON O-RINGS

A series of special tests was performed with O-rings installed on metal fittings; these tests were established to explore the possible failure of LOX system static O-rings as a result of the differing thermal contraction rates between the nitrile elastomer and the metal. Various sizes of



6920-11/21/62-1

Figure 11 . Gaseous Oxygen Exposure Chamber

TABLE 13

SUMMARY OF PHYSICAL PROPERTY DATA: MS28778-16 O-RINGS
AFTER EXPOSURE TO OXYGEN ATMOSPHERE

Condition	Tensile Strength, psi	Compressive Load, pounds, at Deflection, %					
		10	20	30	40	50	60
Control	1483	76	161	292	523	987	2080
Unstressed-Ring in O_2 Atmosphere	1465	71	152	268	466	837	1680
15% Stretched-Ring in O_2 Atmosphere	1450	63	143	262	470	874	1464

intentionally damaged (cut or notched) MS28778 O-rings were installed on a stainless-steel shaft; the unit then was cycled between ambient temperature and liquid nitrogen temperature for a varying number of cycles. O-rings of the MS28778-10 (0.755-inch ID), -12 (0.924-inch ID), and -16 (1.171-inch ID) were subjected to approximately 13, 32 and 44% circumferential stress, respectively, on the shaft. This variation in the inside diameter of rings on the constant-dimension shaft provided an opportunity to investigate the effects of varying O-ring strains (at ambient temperature) on the subsequent cryogenic-temperature contraction behavior.

From the data reported in Table 14, it may be seen that O-rings which had been severely notched (on one or both sides of the O-ring), as well as undamaged control rings, did not break as a result of the cycling. However, breaking did occur in the O-rings which were cut very deeply on one side (50 to 75% of W-diameter) and in those that were cut deeper than 25% of the W-diameter on diametrically opposite sides.

This probably explains why several MS28778 O-rings in LOX service have been found broken upon overhaul of rocket engine systems. Therefore, it is reasonable to state that if an O-ring is cut to an appreciable depth, because of installation mishandling, sharp edges, etc., and the ring then is cycled between ambient and LOX temperature, the ring will break. The combination of the brittle elastomer (at LOX temperatures) and the differential contraction rates between the elastomer and the metal is the cause of such breaking.

Thermal expansion data on butadiene/acrylonitrile copolymers have been obtained by the National Bureau of Standards (Ref. 14). These data are presented in Fig. 12. The recipe for the formulations used is included

TABLE 14

EFFECT OF CRYOGENIC EXPOSURE ON INTENTIONALLY DAMAGED 0-RINGS

0-Ring (On Shaft)	No. of Samples	Description of Damage	No. of Exposure Cycles*	Remarks
MS28778-16	20	None (controls, new rings)	20	No breaks
	10	None (controls, new rings)	10**	No breaks
	4	None (service rings)	4	1 broke
	1	Cut (1/4 depth, 1 side)	8	No break
	1	Cut (1/4 depth, 2 sides)	8	No break
	2	Cut (1/4 depth, 2 sides)	18	No breaks
	1	Cut (1/4 depth, 2 sides)	5	Broke
	2	Cut (1/3 to 1/2 depth, 2 sides)	5	Both broke
	1	Cut (1/2 depth, 1 side)	8	No break
	1	Cut (1/2 depth, 1 side)	17	Broke
	1	Cut (3/4 depth, 1 side)	1	Broke
MS28778-12	2	None (controls, new rings)	7	No Breaks
	3	Notched (1/4 to 1/3 depth, 1 side)	7	No breaks
	3	Notched (1/4 to 1/3 depth, 2 sides)	7	No breaks
	3	Cut (1/2 to 3/4 depth, 1 side)	7	1 broke
MS28778-10	3	None (controls, new rings)	6	No breaks

*Unless otherwise noted, a cycle consisted of 15 minutes in liquid nitrogen and 45 minutes at ambient temperature.

**Cycled 30 minutes in liquid nitrogen, 45 minutes at ambient temperature.

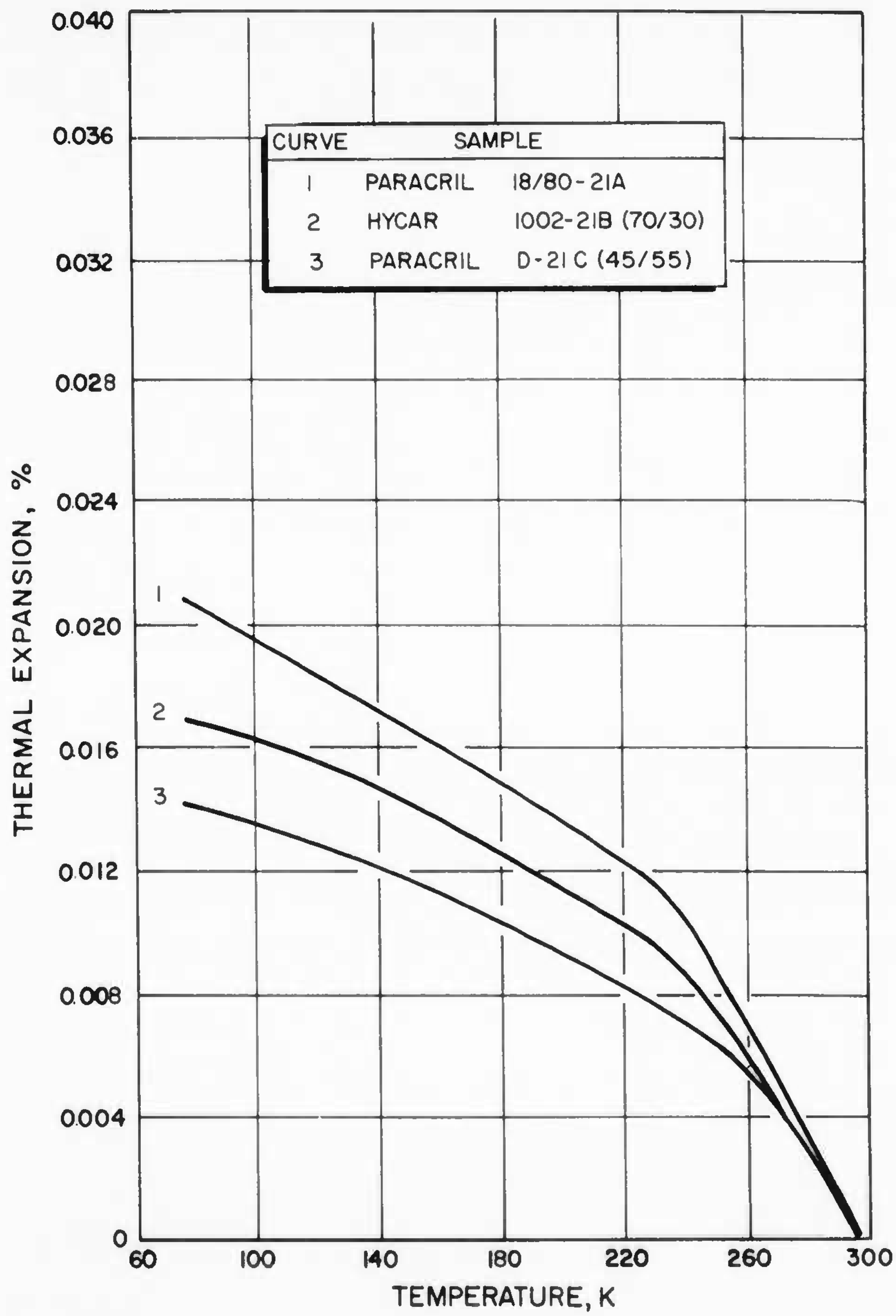


Figure 12. Linear Thermal Expansion Curves for Selected Nitrile Rubber Compounds

in Table 15. The Paracril 18/80 (represents monomer ratio of butadiene and acrylonitrile) compound is an approximation of military specification O-ring compound formulations. However, as the curves indicate, fairly appreciable differences in linear thermal expansion values can arise because of different monomer ratios. Therefore, these curves should be used only as a general guide for anticipating behavior of a nitrile rubber O-ring.

Additional general data on the linear thermal expansion of typical elastomers and common alloys are presented in Table 15.

SUMMARY

Small, but detectable changes occur in the mechanical properties (including low-temperature retraction capabilities) of stressed rings as a result of cyclic exposure to cryogenic temperature (-320 F) in a nonoxidizing environment.

Changes in the mechanical properties of rings are sensitive to the number of cryogenic exposures; larger changes from initial values occurring as the number of cycles is increased. The mechanical properties also may be sensitive to the length of exposure to low temperatures, but this parameter was not investigated in this study.

Observations of changed properties of plasticized rings compared to unplasticized rings, coupled with observations of an oil-like staining of the paper toweling in which cycled O-rings were kept wrapped for approximately 6 months, provide some verification for the hypothesis that plasticizer effects are responsible for the change in O-rings after cryogenic exposure.

TABLE 15

RECIPES FOR NITRILE RUBBER COMPOUNDS USED IN THERMAL EXPANSION STUDY

Compound Designation	Polymer	Estimated Monomer Ratio	Receipe	Parts by Weight	Hardness (Shore-A)
II-21A	Butadiene and Acrylonitrile (Paracril 18-80, Naugatuck Chemical Co.)	80/18	Polymer	100	75
			Zinc Oxide	5	
			Altax (MBTS)	1.5	
			Stearic Acid	1.5	
			Sulfur	1.5	
			FEF Black	50	
			Cure 20 minutes at 310 F		
II-21B	Butadiene and Acrylonitrile (Hycar 1002, B. F. Goodrich Chemical Co.)	70/30	Same as II-21A		75
II-21C	Butadiene and Acrylonitrile (Paracril D, Naugatuck Chemical Co.)	45/55	Same as II-21A		85

Exposure of the O-rings to a 100% gaseous oxygen atmosphere for 10 days at ambient temperature did not affect the materials.

O-rings which have been cut to an appreciable degree and installed on a shaft will break in LOX service. The combination of the brittle elastomer (at LOX temperatures) and the differential contraction ratio between the elastomer and the metal probably would cause such breaks.

TASK 3--EVALUATION OF THE SENSITIVITY OF VARIOUS PROPERTIES TO AGING

Previous studies of elastomer aging have concerned the sensitivity of properties, but have not generally considered those properties involved in the actual functioning of the elastomeric parts. Because evaluating O-rings from rocket engine systems involves testing hundreds of parts, it is important that the evaluation be made rapidly as well as accurately.

Common practice in determining aging in O-rings has been to test for the physical properties which are given in procurement specifications and measured by the manufacturer and purchaser in periodic quality control tests. The sensitivity of these properties (such as tensile strength and hardness) to the aging process is controversial. Tensile strength and hardness properties were included in this test program to determine, with reference to military specifications dealing with nitrile rubber O-ring compounds, their sensitivity to aging. Considerable data are available for comparison. These data were accumulated both by Rocketdyne during rocket engine soft goods analyses, (Ref. 2) and by others studying elastomer aging (Ref. 3 through 8). Tensile strength is easily determined when testing for tensile modulus and elongation, two properties which are known to be age sensitive. Studies made at the National Bureau of Standards (Ref. 15) indicate that ultimate elongation is one of the most useful properties in characterizing the deterioration of rubber vulcanizates. The data obtained indicate that elongation decreases with aging of the rubber. Research at the National Bureau of Standards and at other laboratories (Ref. 16 and 17) has shown that tensile modulus in nitrile compounds increases consistently with aging.

No tensile properties are critical with regard to the actual function of the O-ring except minimum elongation necessary to compensate for installation stretch. The properties studied were those directly connected with the O-ring function; they were correlated where possible with the traditionally determined tensile properties.

The compressive properties of the material used in an O-ring are closely related to the ability of the ring to function properly. The Boeing Airplane Company has conducted studies (Ref. 18) for several years to obtain O-ring design information; these studies indicate that two basic properties must be present in O-ring material: the material must have a sufficient internal force to form a seal and it must be able to withstand the mechanical conditions imposed upon it. Cutting, abrasion, extrusion, and spiraling are caused by the shape, finish, and/or condition of the O-ring gland. Seal life expectancy increases with an increase in compression modulus when no antiextrusion device is used. No information is available concerning the effect of using an antiextrusion device.

The O-ring sealing mechanism was discussed in Ref. 6 . The theory of sealing was elaborated by J. B. Morrison (Ref. 19), who attributed the total effective static sealing force to the sum of the applied fluid pressure and the initial sealing pressure (assuming the absence of extrusion and nominal stress relaxation in the seal). The initial sealing pressure is back pressure resulting from the deflection (compression of the seal when installed),and is therefore a direct function of the compressive modulus of the seal and of the extent to which it is compressed. A simplification of initial sealing pressure is shown in Fig. 13 , and the pressure is indicated as a schematic spring. This spring force plus the fluid pressure gives the eventual sealing force of the assembly. It was demonstrated in Ref. 20 that the sealing force is not uniformly distributed across the seal face but tends to intensify at points A and B and diminish at C. However, this nonuniformity can be neglected for discussion purposes.

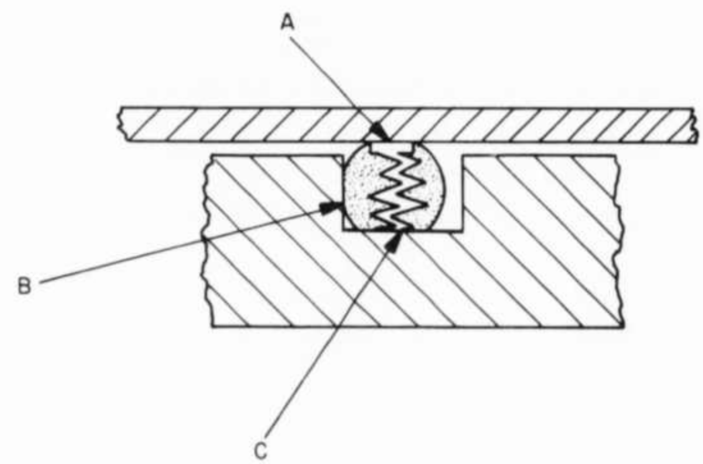


Figure 13. Spring Representation of Initial Sealing Pressure

With the simplified spring configuration,it is apparent that the spring rate will determine the effective sealing force which is additive to the fluid pressure sealed. As long as this spring rate is a positive value, there will be a sealing force in excess of the pressure to be sealed.

If for any reason the spring rate would drop to zero, there would no longer be an effective sealing force and leakage could result. Apparently, when the compression set of an O-ring reaches 100%, the spring rate has dropped to zero because there is no longer a force tending to push the seal surface back to its original configuration; for this reason, the compression-set characteristics may be the most important of the many determinable physical properties.

Rocketdyne has investigated the compressive properties of O-rings (compression set and compressive deflection) because of the apparent close relationship of these properties to the factors involved in the sealing of the rings. As determined in previous studies of O-rings from ballistic missile systems, the compression-deflection property appears to be sensitive to the aging phenomenon.

Another factor closely related to the O-ring sealing mechanism is compression relaxation. Studies (Ref. 21) indicate that tests of this property give a good indication of the ability of an elastomer to exert sufficient internal pressure to form a satisfactory seal.

One of the requirements of an elastomeric seal is that it maintain force against the sealing surface. When a confined O-ring is immersed in a solvent, two phenomena occur which have opposite effects upon the sealing force exerted by the O-ring. The first phenomenon, a swelling pressure which results when the rubber absorbs a solvent (such as trichloroethylene) by solvation of the rubber molecule, tends to increase the sealing force. The second phenomenon, a relaxation caused by a decrease in the compressive modulus of the solvated elastomer, results in a decrease in sealing pressure. The measurements made on confined O-rings represent the net effect of these two opposing forces. When the swell of the O-ring is limited by the confining groove, stress will increase rapidly to a maximum, after which the relaxation effect becomes dominant. The value of the maximum swelling force is affected by both the amount of squeeze and by the allowable swell. While these effects are more pronounced with fluids of high solvent power, they are also present in O-rings used in fuel and oil systems. The sensitivity of compressive relaxation studies in detecting aging effects was therefore investigated.

The sensitive properties to be investigated were measured using Buna-N O-rings supplied by three different manufacturers; they were tested after being aged at 212 F for periods of 1 to 90 days. The sensitivity of the properties to the aging process was determined by analysis of the data obtained. The following discussion of the experimental aging portion of the program includes materials, test procedures, data analysis, and conclusions.

O-RING TEST MATERIALS

Military O-ring specifications are concerned primarily with performance and endurance testing of the rings, without emphasis on the physical properties of the material used. Many specifications state that "the physical property of the material at the time of manufacture shall be suitable for the purpose intended, but irrespective of what the value (the 'as determined'value) may be, it will not be cause for rejection" (Ref. 22). (An exception to this is MIL-R-25897C, covering Viton O-rings, in which minimum physical properties are specified for unaged and aged parts.) Thus, it is not unusual to find large variation in the physical properties of O-rings supplied by different manufacturers in accordance with the same military specification. For example, with reference to MIL-P-5315 (MS29512 and MS29513 O-rings), it may be noted that the permissible tensile strength (taking into account a ±15% allowable variation of the qualification value) of O-rings from qualified suppliers may range from 848 to 2013 psi.

If there are variations in the physical properties of qualified O-rings, it is logical to assume that there are also variations in the aging resistance of O-rings from different suppliers. As discussed in the introduction to this report, the physical properties and resistance to aging of O-rings can be altered dramatically by adding or subtracting certain ingredients in the formulation.

In determining the extent of variation, if any, in the aging resistance of parts from different qualified suppliers, MS29513 O-rings from three manufacturers qualified to MIL-P-5315 were selected for examination. These rings are among the most widely used in ballistic engine systems, and the qualification values of the suppliers approved to this specification were readily available. This permitted selection of the manufacturer with the highest (Precision Rubber Products Corporation) and the lowest (Linear, Inc.) tensile strength values qualified to the specification as well as a manufacturer between the two extremes (Parker Seal Company). Parker O-rings were selected because that company supplies Rocketdyne with O-rings. O-rings from other manufacturers were not included in the program only because of funding limitations, and because it is more meaningful to determine the extent of aging among suppliers with the most divergent property characteristics than to determine the aging resistance of all manufacturers. If appreciable deviations in aging resistance occurred among the three suppliers offering the extremes in properties, the rings from other qualified suppliers could be tested and evaluated in a similar program.

The -218 size O-rings tested in the program had an actual W-diameter of 0.139 ±0.004 inch, an actual inside diameter of 1.234 ±0.006 inch, and a nominal outside diameter equals 1.5 inches. They were selected because of their convenient size for aging and testing.

All O-rings used in the program were selected from a single batch from each manufacturer to eliminate any possible differences in materials or curing conditions. Each O-ring used in the program was examined under 10X magnification to ensure that it was free from surface cuts or defects which might result in premature material failure during property tests.

To determine control values, five samples were run for each test. For all other testing, three samples per test were used unless otherwise noted. The values of properties reported are therefore the average of the three samples tested.

TEST PROCEDURES AND DESCRIPTION

Method A: Hardness

Shore-A hardness readings were made on each O-ring in at least five areas equally spaced about the O-ring circumference. Readings were taken at the ambient temperature (77 ±5 F) approximately 30 minutes after the O-rings were removed from the aging oven. A spring-actuated instrument was used. Values reported in Table 16 represent the average of all readings on the three samples.

Method B: Tensile Properties (Tensile Stress, Ultimate Elongation, Tensile Strength)

The tensile test series was conducted in accordance with the ASTM method for tension testing of rubber O-rings: ASTM D 1414-56T. An Instron universal testing machine was utilized to apply and measure the load (and the elongation). Tests were performed at ambient temperature (77 ±5 F) at a crosshead speed of 20 in./min. The O-ring samples were tested within 30 minutes to 2 hours after their removal from the aging oven.

Tensile stress (at 50%, 100%, and 150% elongation), tensile strength, and ultimate elongation were determined on each O-ring and calculated as specified in ASTM D 1414-56T, using the actual O-ring sample dimensions at the time of the test.

Method C: Compressive Properties (Compression Set, Compressive Stress, Compressive Relaxation)

Compression-set tests were performed in accordance with ASTM D 395-61, Method B (compression set under constant deflection), except that O-ring samples were used in place of compression-set buttons. The compression set is expressed as a percentage of the original deflection, and is calculated as follows:

$$C = \frac{t_o - t_f}{t_o - t_s} \times 100$$

TABLE 16

EFFECT OF AGING ON PROPERTIES OF

Supplier	Aging Period At 212 F, Days	W-Diameter		Hardness		Tensil		
		Inch	% Change	Shore-A Points	% Change	50%	% Change From Start	100%
Linear	0	0.1363	0	65.5	0	216	0	388
	1	0.1364	0	65.6	0	236	9.3	429
	3	0.1360	0	68.0	3.8	264	22.2	480
	5	0.1357	0	66.3	1.2	261	20.8	482
	10	0.1360	0	70.8	8.1	307	42.1	621
	20	0.1350	-0.74	71.2	8.7	357	65.3	677
	30	0.1349	-0.74	74.8	14.2	410	90.0	825
	40	0.1348	-0.74	77.3	18.0	458	112	987
	50	0.1353	-0.74	78.0	19.1	569	163.5	1219
	60	0.1350	-0.74	80.0	22.2	683	216	1452
	70	0.1351	-0.74	82.1	25.4	839	288	----
	80	0.1353	-0.74	83.83	28.0	988	356	----
	90	0.1351	-0.74	85.83	31.0	1133	424	----
Parker	0	0.1350	0	60.5	0	176	0	336
	1	0.1338	-0.74	65.1	7.6	220	25	449
	3	0.1338	-0.74	66.1	9.25	237	34.6	481
	5	0.1337	-0.74	65.8	8.75	240	36.4	503
	10	0.1334	-0.74	69.0	14.1	237	34.6	508
	20	0.1333	-1.5	74.6	23.3	461	162	998
	30	0.1329	-1.5	79.7	31.7	643	265	1398
	40	0.1330	-1.5	85.2	40.8	1008	473	----
	50	0.1331	-1.5	85.8	41.7	1379	684	----
	60	0.1330	-1.5	87.3	44.2	1405	689	----
	70	0.1326	-2.2	88.3	46.1	----	----	----
	80	0.1326	-2.2	89.3	47.6	----	----	----
	90	0.1320	-2.2	93.5	54.6	----	----	----
Precision	0	0.1365	0	60.2	0	160	0	323
	1	0.1343	-2.2	59.0	2.0	175	9.35	372
	3	0.1344	-2.2	63.8	6.0	210	31.2	487
	5	0.1338	-2.2	63.5	5.5	224	40.0	519
	10	0.1336	-2.2	66.5	10.5	216	35.0	505
	20	0.1328	-2.2	70.2	16.6	366	128.5	843
	30	0.1313	-4.4	74.5	23.8	521	226	1163
	40	0.1308	-4.4	79.2	31.6	663	314	1460
	50	0.1300	-5.1	81.0	34.6	791	394	1690
	60	0.1310	-4.4	83.3	38.4	920	475	1985
	70	0.1312	-4.4	85.8	42.6	1330	734	----
	80	0.1312	-4.4	87.5	45.4	1758	1000	----
	90	0.1303	-5.1	89.67	49.0	1653	935	----

TABLE 16

EFFECT OF AGING ON PROPERTIES OF O-RINGS (MS29513-218)

ss	Tensile Stress, psi						Tensile Strength		Ultimate Elongation	
% Change	50%	% Change From Start	100%	% Change From Start	150%	% Change From Start	psi	% Change	5%	% Change
0	216	0	388	0	622	0	1141	0	253	0
0	236	9.3	429	10.6	707	13.7	1173	+2.8	228	-9.9
3.8	264	22.2	480	23.7	793	27.5	1113	-2.5	203	-19.8
1.2	261	20.8	482	24.3	794	27.6	1178	+3.2	209	-17.4
8.1	307	42.1	621	60.3	1035	66.3	1137	-0.4	170	-32.8
8.7	357	65.3	677	74.7	1127	81.1	1127	-1.2	150	-40.7
14.2	410	90.0	825	113	----	----	1345	+18	140	-44.6
18.0	458	112	987	155	----	----	1310	+15	128	-49.4
19.1	569	163.5	1219	215	----	----	1598	+40	129	-49.0
22.2	683	216	1452	275	----	----	1555	+36	106	-58.1
25.4	839	288	----	----	----	----	1615	+41	91	-64.1
28.0	988	356	----	----	----	----	1613	+41	72	-71.5
31.0	1133	424	----	----	----	----	1795	+57	76	-70.0
0	176	0	336	0	603	0	1797	0	355	- 0
7.6	220	25	449	33.6	840	39.4	1872	+4.2	280	-21.2
9.25	237	34.6	481	43.2	824	36.8	1783	-0.8	279	-22.4
8.75	240	36.4	503	49.7	928	54.0	1855	+3.2	228	-35.8
14.1	237	34.6	508	51.2	936	55.4	2063	+15	275	-22.7
23.3	461	162	998	197	1515	151	1817	+1.1	199	-44.0
31.7	643	265	1398	317	----	----	2013	+12	146	-58.9
40.8	1008	473	----	----	----	----	1950	+8.5	91.8	-74.1
41.7	1379	684	----	----	----	----	1843	+2.6	66	-81.5
44.2	1405	689	----	----	----	----	2160	+20	74	-79.3
46.1	----	----	----	----	----	----	1894	+5.4	50	-86.0
47.6	----	----	----	----	----	----	1875	+4.3	49	-86.3
54.6	----	----	----	----	----	----	1528	-15	26	-92.6
0	160	0	323	0	618	0	1860	0	325	0
2.0	175	9.35	372	15.2	733	18.6	1777	-4.5	278	-14.5
6.0	210	31.2	487	50.7	953	54.3	2057	+11.6	260	-20.0
5.5	224	40.0	519	60.6	1005	62.6	2055	+10.5	253	-22.2
10.5	216	35.0	505	56.4	998	61.6	2182	+17	281	-13.6
16.6	366	128.5	843	161	1513	145	1873	+0.7	177	-45.6
23.8	521	226	1163	260	1990	222	2377	+23	178	-45.4
31.6	663	314	1460	351	----	----	2077	+12	137	-57.9
34.6	791	394	1690	422	----	----	2357	+27	138.5	-57.4
38.4	920	475	1985	515	----	----	2428	+31	123	-62.2
42.6	1330	734	----	----	----	----	2567	+38	96	-70.5
45.4	1758	1000	----	----	----	----	2407	+29	77	-76.5
49.0	1653	935	----	----	----	----	2507	+35	71	-78.1

where

C = compression set expressed as a percent of original deflection (approximately 25%)

t_o = original W-diameter

t_f = W-diameter after test

t_s = thickness of the spacer bar used

Compressive stress tests (compression-deflection) used an Instron universal testing machine to compress the O-rings up to 30% deflection. The rate of loading was 0.02 in./min.

Compressive relaxation tests were performed by compressing the O-rings which had been used in the compressive stress tests to a fixed 20% deflection utilizing the Instron machine. The change in load over a predetermined interval was recorded on the Instron strip recorder chart.

The compression relaxation values reported represent the slope of the stress decay curve. It is calculated from the following equation:

$$\text{Slope} = \frac{(S_t/S_o)_{30} - (S_t/S_o)_{300}}{\log(t)_{30} - \log(t)_{300}}$$

where

$(S_t/S_o)_{30}$ = ratio of stress at 30 seconds to initial stress

$(S_t/S_o)_{300}$ = ratio of stress at 300 seconds to initial stress

$(t)_{30}$ = 30 seconds

$(t)_{300}$ = 300 seconds

All of the compressive test measurements were made at 77 ±5 F. The stress and relaxation tests were performed no sooner than 1 hour after removal of the samples from the aging oven.

Method D: Dimensions

W-diameter measurements were made on each O-ring in at least five areas equally distributed around the circumference of the O-ring. A dead-weight instrument graduated in increments of 0.0010 inch was used. The inside diameter of each ring was determined using a stepped cone.

ACCELERATED AGING PROCEDURES

To observe the sensitivity of properties with aging, it was necessary to induce aging effects in the O-ring materials. This was done by using accelerated aging techniques. The accelerated aging was done in a Konrad oven equipped with a recorder controller. The oven was calibrated prior to the test program and the temperature variation within the oven was found to be less than ±5 F.

The selection criteria of the oven aging method for accelerated aging of O-rings are discussed in Task 4.

ANALYSIS OF DATA

The data obtained during O-rings aging studies are given in Tables 16, 17, and 18. The values presented represent average values of five samples for the control data and of three samples for the aging data.

Various methods of presenting and analyzing the accelerated aging data were employed to find relationships among the measured variables. Because the usual tabular and graphic methods indicated that any relationships among the variables were quite complex, a computerized statistical data analysis technique was used.

COMPUTER ANALYSIS OF ACCELERATED AGING DATA

The general procedure in a computer analysis program is to use a regression analysis technique based upon a stepwise regression program written for handling problems of this nature. Basically, the technique involves fitting a least-squares polynominal in certain variables to an observed quantity. For example, a polynominal of the form $y = a + bt + ct^2$ could be attempted where y might represent the elongation and t the aging time. The regression procedure would then decide which, if any, of the three terms has a significant effect on elongation and would provide estimates of the constants a, b, and c for these terms. The program would then specify a multiple correlation coefficient for the fit, providing a measure of the over-all correlation of the terms in the equation to the elongation. As the multiple correlation coefficient approaches one, the prediction afforded by the equation becomes more accurate. In addition, the standard error of estimate is specified. This quantity is simply the standard deviation of the differences of the predicted and observed values of the property under consideration. Thus, a good fit is characterized by a small standard error of estimate.

TABLE 17

EFFECT OF AGING ON COMPRESSIVE PROPERTIES O

Supplier	Aging Period at 212 F, Days	10 Through 50 % Deflection Under Compress					
		10%	% Change	20%	% Change	30%	% Change
Linear	0	24	0	66	0	131	0
	1	26	8.32	70	6.6	141	7.64
	3	23	-4.16	68	3.04	142	8.4
	5	29	20.8	79	19.8	162	23.7
	10	26	8.32	73	10.6	149	13.8
	20	33	37.5	92	39.5	191	45.9
	30	37	54.1	101	53.3	210	60.4
	--	36	50.0	99	50.2	205	56.5
	50	34	41.6	98	48.7	199	51.9
	60	47	95.9	135	105	277	112
	70	57	137.5	168	155	391	199
	80	58	142	163	147	357	173
	--	63	163	199	202	464	254
Parker	0	17	0	46	0	94	0
	1	21	23.5	57	23.8	120	27.7
	3	22	29.4	59	28.2	126	34.1
	5	25	47.0	63	36.9	131	39.4
	10	24	41.2	62	34.8	128	36.2
	20	35	106	98	113	221	135
	30	39	129	116	152	262	179
	--	38	124	116	152	289	208
	50	37	118	117	154	289	208
	60	74	335	229	398	534	469
	70	96	465	321	598	778	728
	80	93	447	291	533	700	647
	--	115	577	417	807	1032	997
Precision	0	16	0	46	0	100	0
	1	19	18.8	50	8.69	101	1.0
	3	20	25.0	56	21.7	118	18
	5	24	50.0	60	30.4	126	26
	10	22	37.6	59	28.2	122	22
	20	27	68.8	77	67.3	167	67
	30	35	119	94	104	204	104
	--	32	100	91	97.7	200	100
	50	36	125	103	124	233	133
	60	65	306	184	300	398	298
	70	91	470	275	500	651	551
	80	85	431	243	427	610	510
	--	96	500	296	545	714	614

TABLE 17

ECT OF AGING ON COMPRESSIVE PROPERTIES OF O-RINGS (MS29513-218)

Through 50 % Deflection Under Compressive Load, pounds								Negative Compression Relaxation Slope
20%	% Change	30%	% Change	40%	% Change	50%	% Change	
66	0	131	0	287	0	654	0	0.0528
70	6.6	141	7.64	265	-7.65	513	-21.6	0.0205
68	3.04	142	8.4	279	-2.8	563	-13.96	0.0258
79	19.8	162	23.7	307	6.96	601	-8.1	0.0179
73	10.6	149	13.8	288	0.348	602	-7.96	0.0056
92	39.5	191	45.9	377	31.3	762	16.6	0.0191
101	53.3	210	60.4	413	43.8	771	17.9	0.0154
99	50.2	205	56.5	491	71	1009	54.5	-----
98	48.7	199	51.9	449	56.5	918	40.5	0.0238
135	105	277	112	547	90.5	1092	67	0.0304
168	155	391	199	866	205	1616	147	0.0315
163	147	357	173	749	161	1402	115	0.0356
199	202	464	254	930	224	1872	187	------
46	0	94	0	191	0	407	0	0.0231
57	23.8	120	27.7	244	27.8	521	28.2	0.0261
59	28.2	126	34.1	264	38.2	556	36.8	0.0311
63	36.9	131	39.4	267	39.8	583	43.6	0.0309
62	34.8	128	36.2	258	35.1	584	41.3	0.0225
98	113	221	135	481	152	1045	157	0.0247
116	152	262	179	579	203	1050	158	0.0366
116	152	289	208	900	372	2055	407	------
117	154	289	208	1127	490	2593	294	0.0521
229	398	534	469	1200	528	2600	296	0.0483
321	598	778	728	1703	795	3670	784	0.0519
291	533	700	647	1709	796	3713	820	0.0613
417	807	1032	997	2235	1070	4595	1030	------
46	0	100	0	222	0	492	0	0.0273
50	8.69	101	1.0	203	-8.05	430	-12.6	0.0361
56	21.7	118	18	247	11.2	558	13.4	0.0330
60	30.4	126	26	257	15.8	548	11.4	0.0359
59	28.2	122	22	255	14.8	532	8.14	0.0286
77	67.3	167	67	350	57.5	607	23.4	0.0415
94	104	204	104	393	76.9	717	45.8	0.0485
91	97.7	200	100	644	190	1759	258	------
103	124	233	133	782	252	1937	294	0.0473
184	300	398	298	801	261	1623	230	0.0507
275	500	651	551	1399	530	3273	566	0.0577
243	427	610	510	1275	475	2383	385	0.0548
296	545	714	614	1565	606	3483	607	------

TABLE 18

COMPRESSION SET VALUES

Aging Period, Days	Compression, %		
	Parker	Linear	Precision
2.9 (70 hours)	15.2	12.3	14.5
5	17.0	13.8	16.0
5.9 (140 hours)	17.9	14.8	17.4
8.8 (210 hours)	21.1	17.7	20.6
10	21.8	18.1	20.4
14	25.0	20.4	23.4
20	29.4	23.0	28.2
25	30.2	24.0	28.2
31	32.4	26.1	30.6

The printout of the differences between the actual and the predicted quantities demonstrates the usefulness of the model. A series of graphs provides the analyst with a picture of the adequacy of the derived model in relation to the actual data. The primary problem encountered in using the technique is that there is no theoretical basis for specifying the form of the equation which describes O-ring behavior. Fortunately, polynomials can be used to approximate any well-behaved function over a finite range, and they can be used in this program.

In the preliminary investigation of the data, the computer was programmed to provide general relationships among the variables and one over-all equation for all manufacturers for each variable. This first attempt at model-fitting included, in addition to variables such as time (to degree five), a special "check" function: time times manufacturer. The presence of this artificial function (in which each of the manufacturers is assigned a purely arbitrary numerical value) in the derived relationships indicates that the aging of O-rings is affected differently by different manufacturers, and that to provide one over-all equation (and curve) for each variable regardless of manufacturer, a complex function composed of some parameter related to the O-ring manufacturer would have to be included in the model.

It was more beneficial to the program to attempt correlations and to develop models for the variables for each manufacturer separately than to continue to develop complicated and unwieldy equations. This approach to the analysis of the data employed models based upon polynominals (in aging time to degree five) for the data from each of the three manufacturers to provide relationships for the various characteristic properties measured. Subsequently, the square root function was also considered, and improved some of the models considerably. The models obtained appear encouraging and the similarity of the models for the different manufacturers supports the belief that they are meaningful. Table 19 gives the relationships obtained for the various properties included in the analysis program, the multiple correlation coefficient, standard error of estimate for the model, and a qualitative rating of the usefulness of the model and the data fit based upon a consideration of the experimental factors involved in obtaining that data.

Only a limited number of properties were included in this analysis program. Thus, the omission of relationships in the table for several variables for the different manufacturers indicates only that the variable was not considered, not that no relationship exists. In addition, only two basic mathematical models were formulated and included in the computer program. These were the polynomial function (to degree five) and the polynomial function with an additional square-root term included.

No statistical statements about the adequacy of the obtained models are available because no theoretical basis for the models has yet been found and because the data analyzed represent average values of the original data. The first reason is the most important and presents the most difficulty. Aging data from this and other studies (Ref. 15, 23, and 24) indicate that there may be two distinct periods of aging: an initial induction period and a secondary aging period. Thus, it may be necessary to fit two or more models to the data, rather than attempting an over-all fit using one model.

TABLE 19

MATHEMATICAL RELATIONSHIPS AM

Property	Manufacturer	Variables Considered	General Relation	
W-diameter	Linear	1. T, T^2, T^3, T^4, T^5, constant	1. $f(T, T^2)$	1
		2. No. 1 + $\sqrt{T}$	2. $f(\sqrt{T}, T^3)$	2
	Parker	Same as No. 1	$f(T)$	
	Precision	Same as No. 2	$f(T, \sqrt{T})$	
Shore-A Hardness	Linear	3. T, T^2, T^3, T^4, T^5, constant	3. $f(T, T^2)$	3
		4. No. 3 + $\sqrt{T}$	4. $f(T, \sqrt{T}$	4
	Parker	Same as No. 3	$f(T, T^4, T^5,$	
	Precision	Same as No. 4	$f(T, \sqrt{T})$	
Elongation	Linear	5. T, T^2, T^3, T^4, T^5, constant	5. $f(T, T^2, T^3, T^4)$	5
		6. No. 5 + $\sqrt{T}$)	6. $f(\sqrt{T})$	
				6
	Precision	Same as No. 6	$f(\sqrt{T})$	
50% Tensile Stress	Linear	7. T, T^2, T^3, T^4, T^5, constant	7. $f(T, T^3)$	7
		8. No. 7 + $\sqrt{T}$	8. $f(T^4, T^5, \sqrt{T})$	8
	Precision	Same as No. 8	$f(T)$	
Tensile Strength	Linear	9. T, T^2, T^3, T^4, T^5, constant	9. $f(T)$	9.
		10. No. 9 + $\sqrt{T}$	10. $f(T)$	10.
	Parker	Same as No. 10	f (constant)	
	Precision	Same as No. 10	$f(\sqrt{T})$	
10% Compressive Stress	Linear	11. T, T^2, T^3, T^4, T^5, constant	11. $f(T^2)$	11.
		12. No. 11 + $\sqrt{T}$	12. $f(T^2)$	12.
		13. W, H, 50 TM, 100 TM, 150 TM, TS, E, + No. 12	13. f(50% TM, TS)	13.

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TABLE 19

MATHEMATICAL RELATIONSHIPS AMONG PROPERTIES

	General Relation	Derived Equation	Multiple Correlation Coefficient	Standard Error of Estimate	Quality of Fit
t	1. $f(T, T^2)$	1. $W = 136.1 - 0.39T + 0.32T^2$	0.924	0.212	Very Good
	2. $f(\sqrt{T}, T^3)$	2. $W = 136.2 + 0.00096T^3 - 0.62\sqrt{T}$	0.939	0.191	Very Good
	$f(T)$	$W = 133.97 - 0.21T$	0.803	0.518	Good
	$f(T, \sqrt{T})$	$W = 136.26 + 0.7T - 4.01\sqrt{T}$	0.954	0.70	Good
t	3. $f(T, T^2)$	3. $H = 66.27 + 2.87T - 0.08T^2$	0.991	1.0	Very Good
	4. $f(T, \sqrt{T}$	4. $H = 65.47 + 1.39T + 2.65\sqrt{T}$	0.992	0.979	Very Good
	$f(T, T^4, T^5,$	$H = 63.06 + 6.15T - 0.0216T^4 + 0.002T^5$	0.997	0.977	Very Good
	$f(T, \sqrt{T})$	$H = 58.64 + 1.08T + 7.38\sqrt{T}$	0.996	1.12	Good
t	5. $f(T, T^2, T^3, T^4)$	5. $E = 242.4 - 97.97T + 33.96T^2 - 5.08T^3 + 0.25T^4$	0.994	7.62	Fair
	6. $f(\sqrt{T})$	6. $E = 242.2 - 57.17\sqrt{T}$	0.988	9.24	Good
	$f(\sqrt{T})$	$E = 309.36 - 80\sqrt{T}$	0.993	10.42	Fair to Good
t	7. $f(T, T^3)$	7. 50% TM = $234.35 + 53.78T + 0.6T^3$	0.998	17.97	Poor to Fair
	8. $f(T^4, T^5, \sqrt{T})$	8. 50% TM = $206.3 + 0.345T^4 - 0.027T^5 + 100\sqrt{T}$	0.999	8.80	Fair to Good
	$f(T)$	50% TM = $185.92T$	0.968	144.86	Very Poor
t	9. $f(T)$	9. TS = $1106.78 + 72.15T$	0.960	70.62	Poor
	10. $f(T)$	10. TS = $1106.78 + 72.15T$	0.960	70.62	Poor
	f (constant)	TS = 1865.58	0	149.2	Very Poor
	$f(\sqrt{T})$	TS = $1812.5 + 231\sqrt{T}$	0.873	140.8	Very Poor
t	11. $f(T^2)$	11. 10% CS = $27.26 + 0.49T^2$	0.964	3.85	Fair to Good
	12. $f(T^2)$	12. 10% CS = $27.26 + 0.49T^2$	0.964	3.85	Fair to Good
	13. f(50% TM, TS)	13. 10% CS = 0.034 (50% TM)+ 0.0149 TS	0.967	3.70	Fair to Good

TABLE 19
(Continue

Property	Manufacturer	Variables Considered	General Relation
10% Compressive Stress (Continued)	Parker	Same as No. 11	f (T^2)
		Same as No. 13	f $(\sqrt{T})$
		14. Same as No. 13 + mandatory 50% TM, TS	14. f $(\sqrt{T}, T^2,$ 50% TM, TS)
	Precision	Same as No. 12	f (T^2)
		Same as No. 13	f (50% TM, TS)
Log (10% Compressive Stress)	Linear	15. T, T^2, T^3, T^4, T^5, constant	15. f (T)
		16. No. 17 + $\sqrt{T}$	16. f (T)
	Parker	Same as No. 15	f (T)
	Precision	Same as No. 16	f (T)

TABLE 19
(Continued)

	General Relation	Derived Equation	Multiple Correlation Coefficient	Standard Error of Estimate	Quality of Fit
	$f(T^2)$	10% CS = $22.95 + 1.18T^2$	0.973	8.13	Poor to Fair
	$f(\sqrt{T})$	10% CS = $23.61\sqrt{T}$	0.689	12.3	Poor
	14. $f(\sqrt{T}, T^2,$ 50% TM, TS)	14. 10% CS = -0.07 (50% TM) + 0.016 TS + $2.65T^2 + 17.48\sqrt{T}$	0.997	1.75	Very Good
	$f(T^2)$	10% CS = $20.91 + 1.04T^2$	0.964	8.44	Poor to Fair
	f (50% TM, TS)	10% CS = 0.048 (50% TM) + 0.0049 TS	0.962	8.58	Fair
stant	15. f (T)	15. Log (10% CS) = 3.20 + 0.105T	0.966	0.094	Very Good
	16. f (T)	16. Log (10% CS) = 3.20 + 0.105T	0.966	0.094	Very Good
	f (T)	Log (10% CS) = 3.002 + 0.195T	0.971	0.162	Good
	f (T)	Log (10% CS) = 2.90 + 0.1922T	0.970	0.163	Good

The second reason is eliminated by considering the original data directly. Averages were used because it was necessary to reduce the amount of data handled in the analysis before machine computation was used. In machine analysis, all of the original data can be easily handled. Because of time and funding limitations, this computer approach could not be explored in depth. Further work in this area could provide meaningful relationships among the variables in relation to aging.

GRAPHICAL PRESENTATIONS

General trends among some of the variables as a function of aging time are given in Fig. 14 through 25.

The following discussion of the various properties evaluated in this study covers three topics:

1. The general characteristics of the property as a function of age
2. The sensitivity of the property to age and the practical usefulness of the property in O-ring aging studies
3. The differences in the aging characteristics of the property as a function of the O-ring manufacturer

W-DIAMETER

The W-diameter of the O-ring decreases slightly with age. The absolute change and percentage change (from the initial value) vary with the O-ring manufacturer. The greatest change occurred with the Precision O-rings;

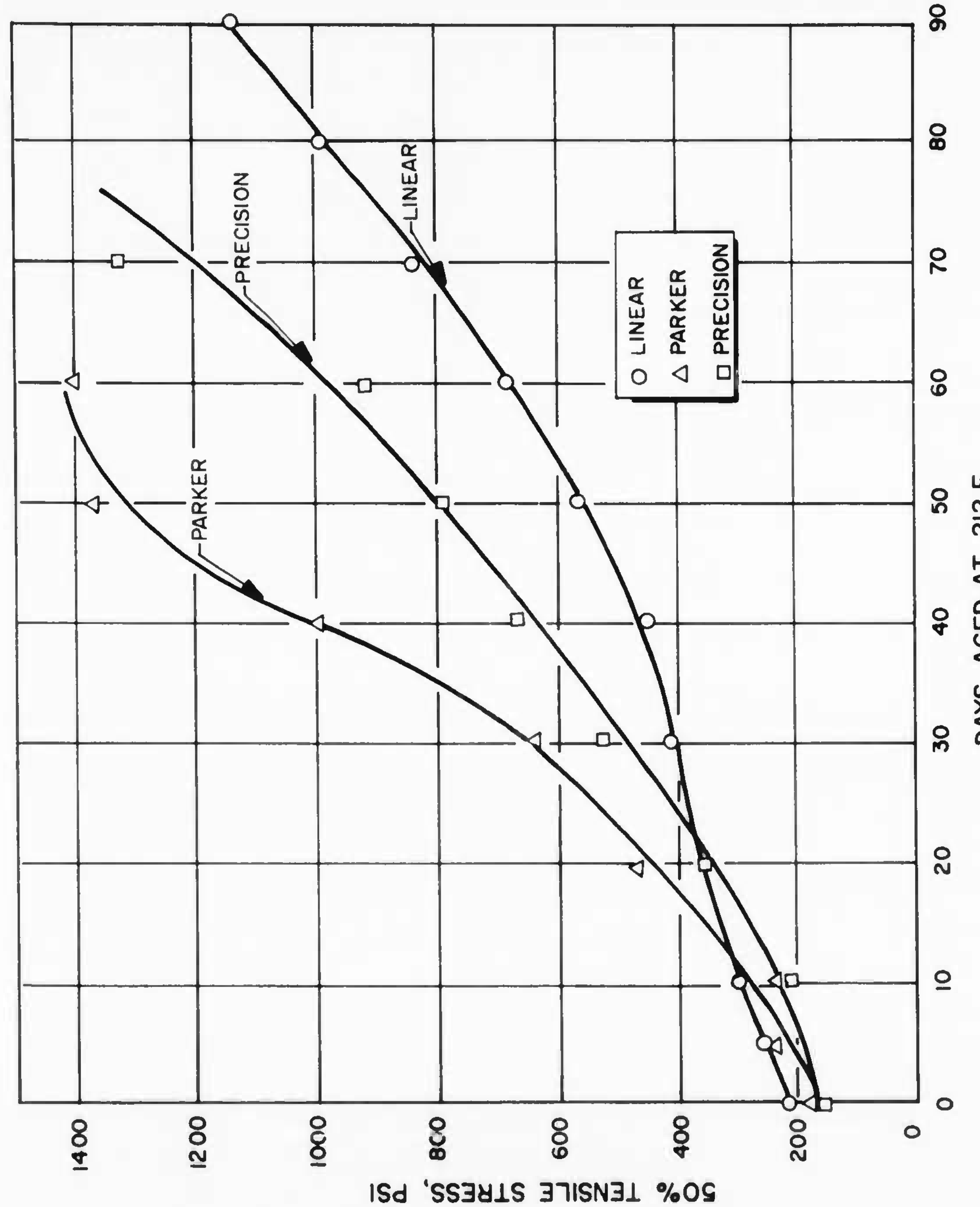


Figure 14. 50% Tensile Stress vs Aging Time

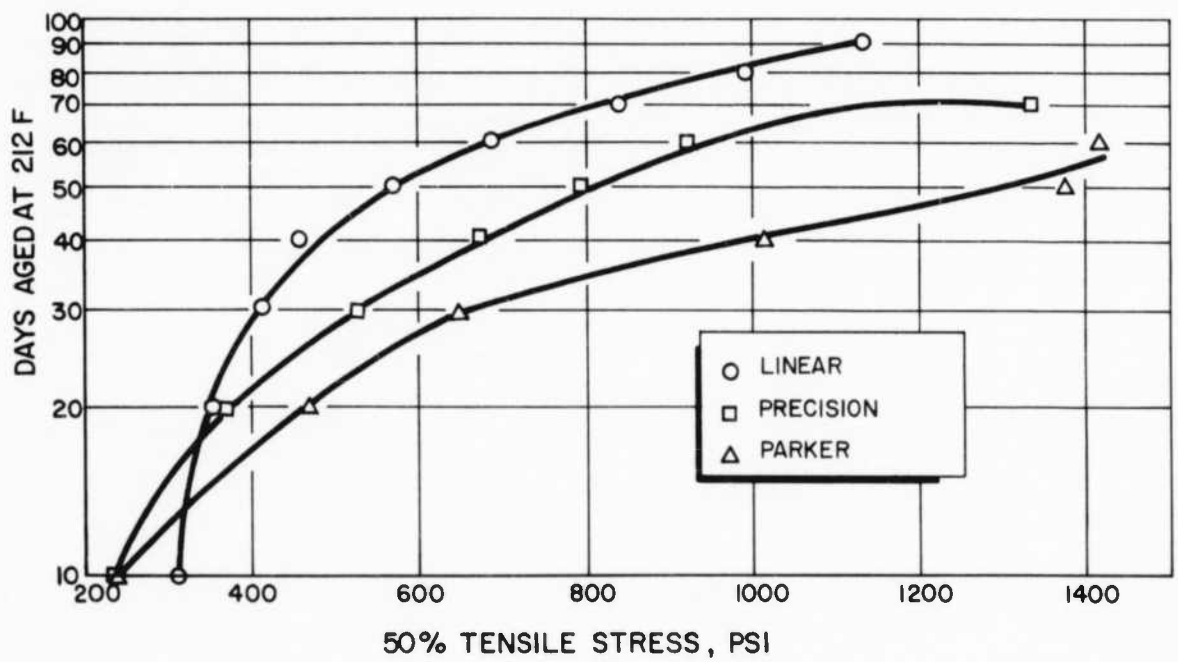


Figure 15 . Log (Aging Time) vs 50% Tensile Stress

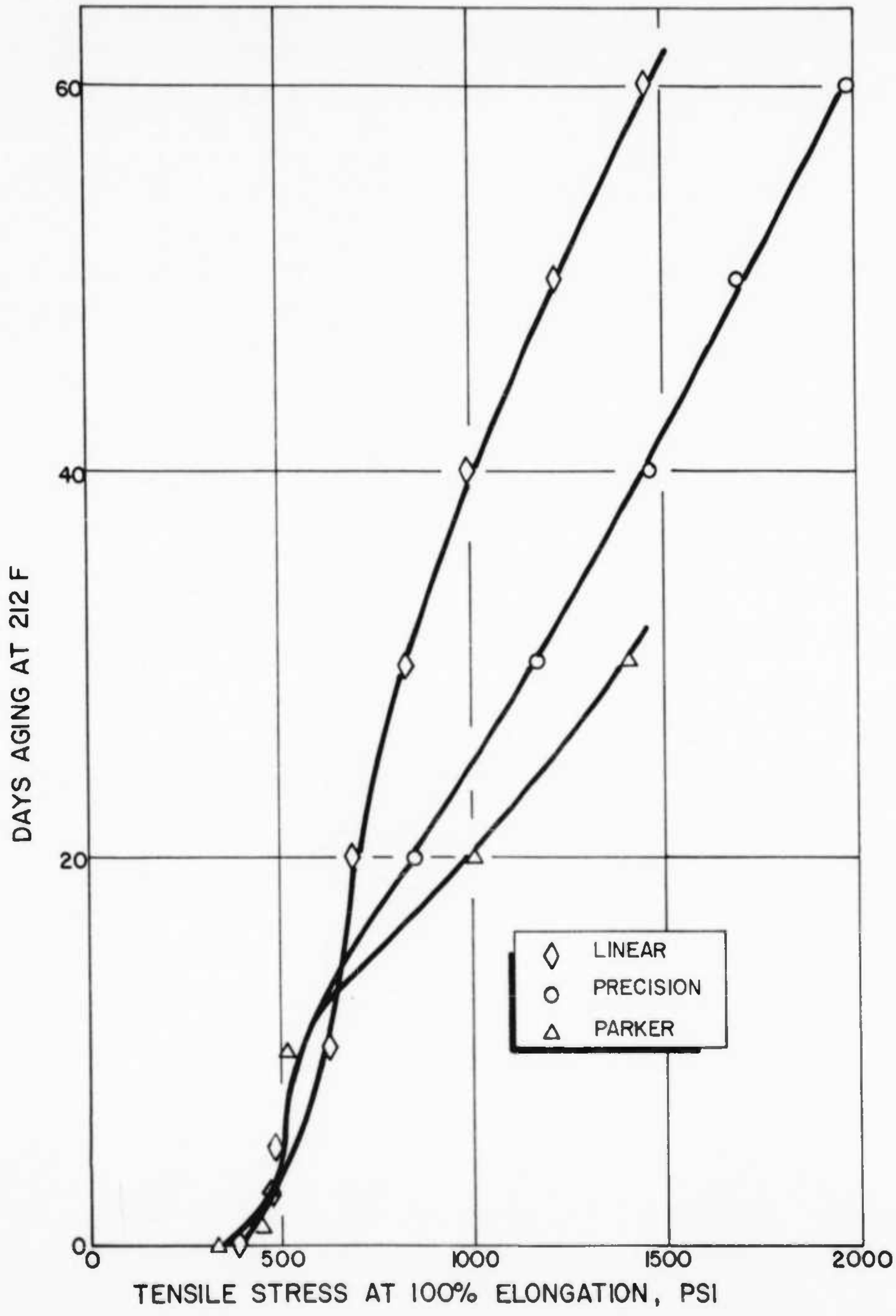


Figure 16 . Effect of Aging on 100% Tensile Stress

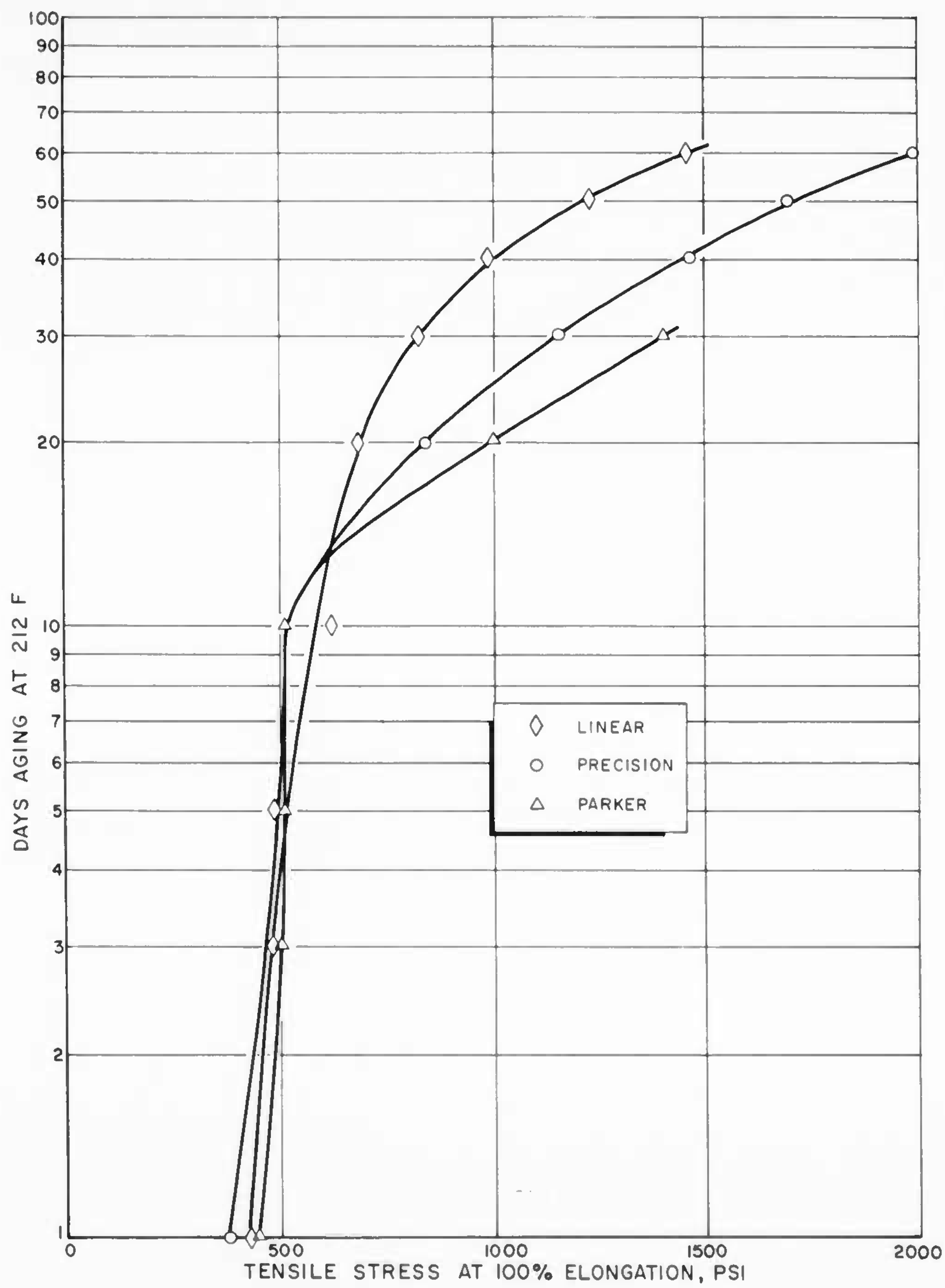
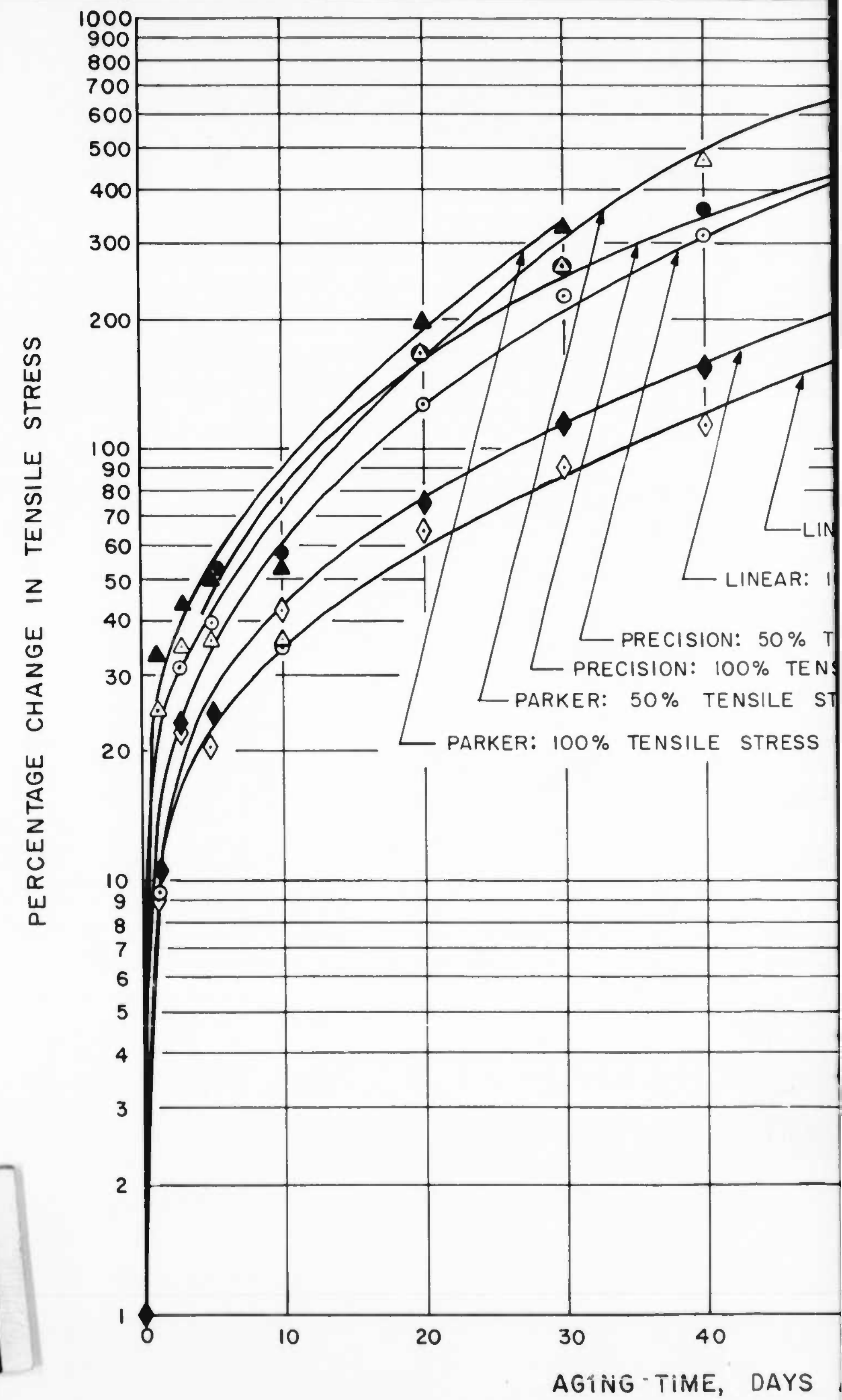


Figure 17. Aging Time vs 100% Tensile Stress



R-5253

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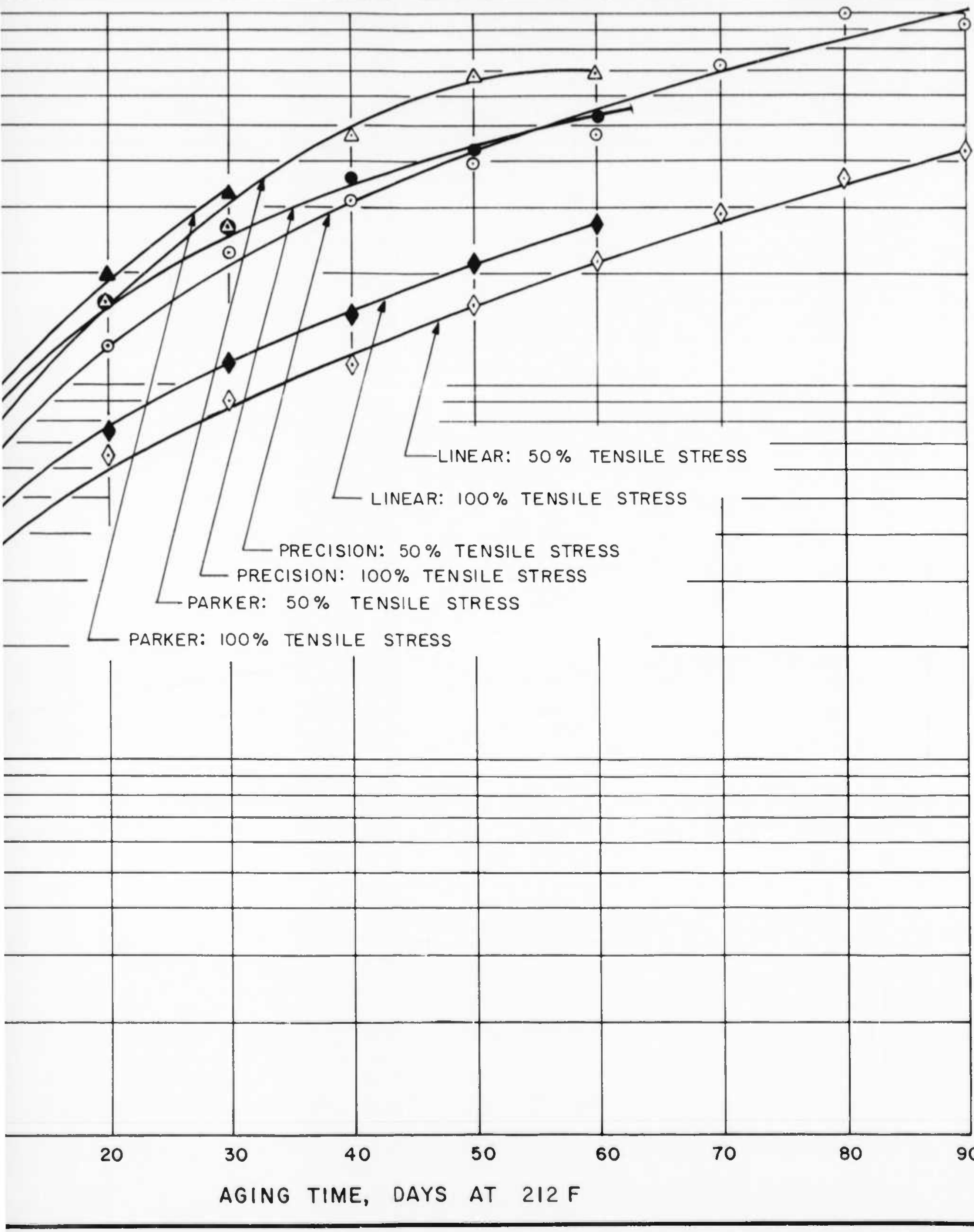


2

Figure 18. Percentage
50 and 100
Stress vs

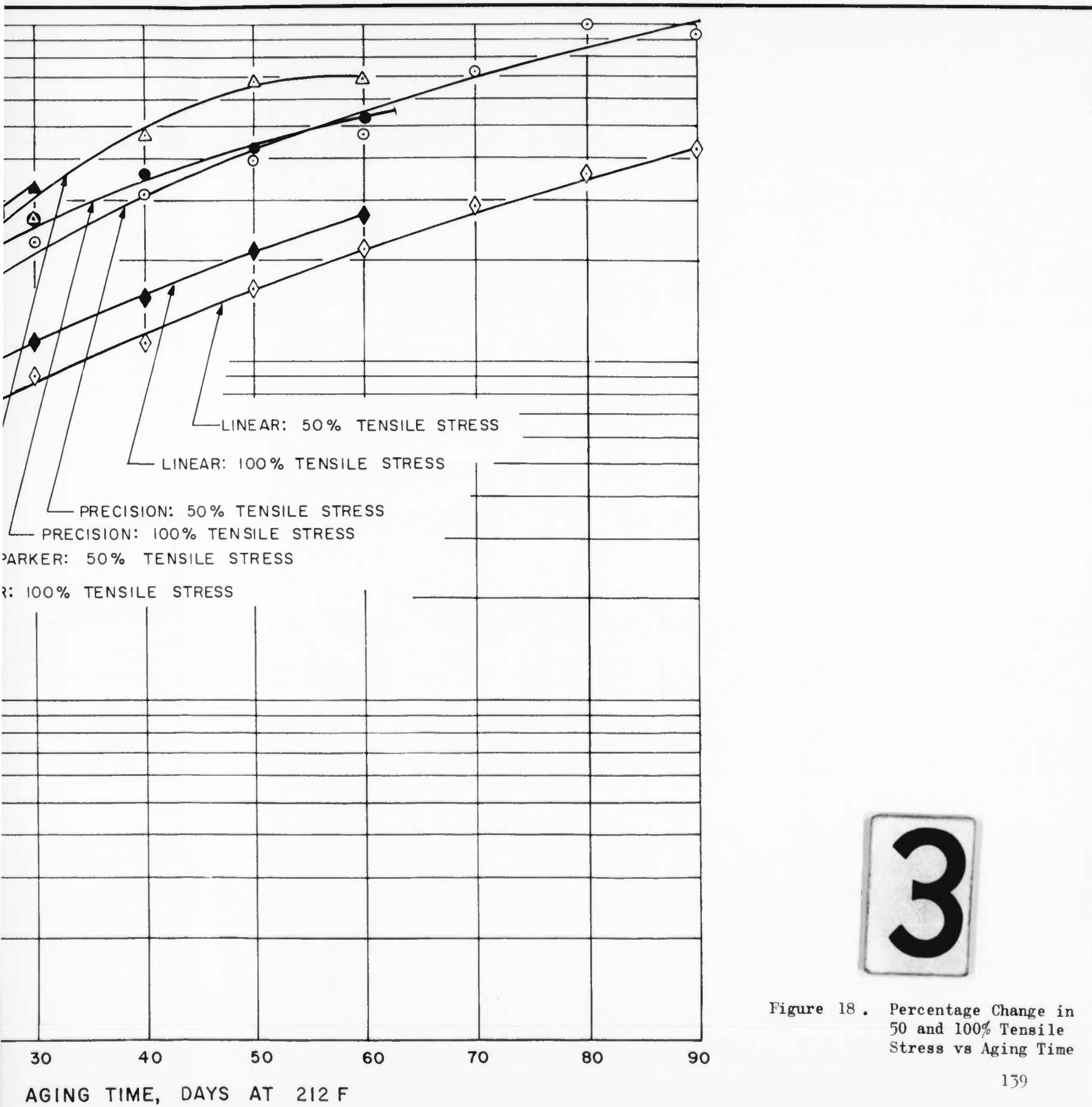
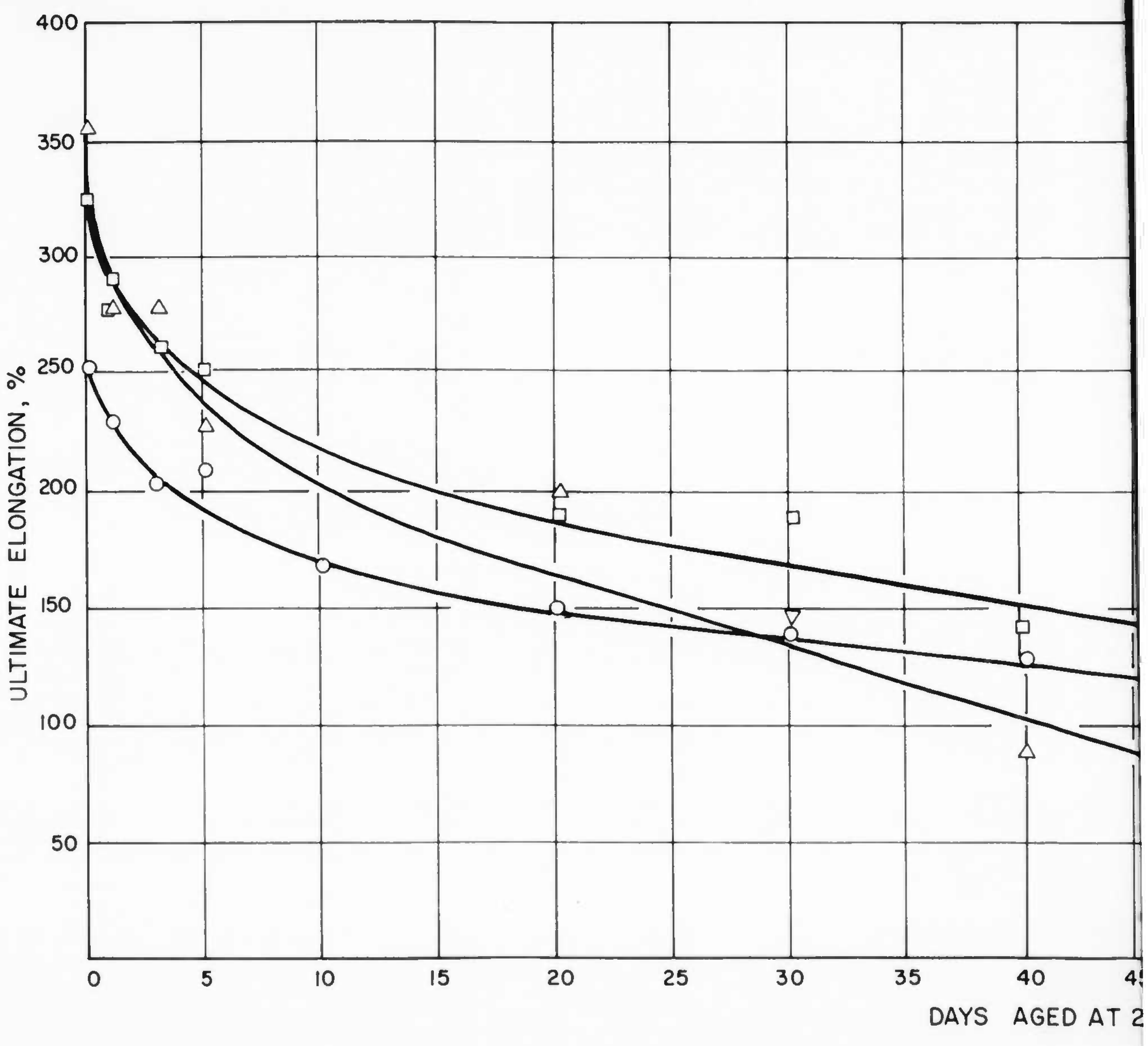


Figure 18. Percentage Change in 50 and 100% Tensile Stress vs Aging Time


ULTIMATE ELONGATION, %
400
350
300
250
200
150
100
50
0
5
10
15
20
25
30
35
40
DAYS AGED AT 2

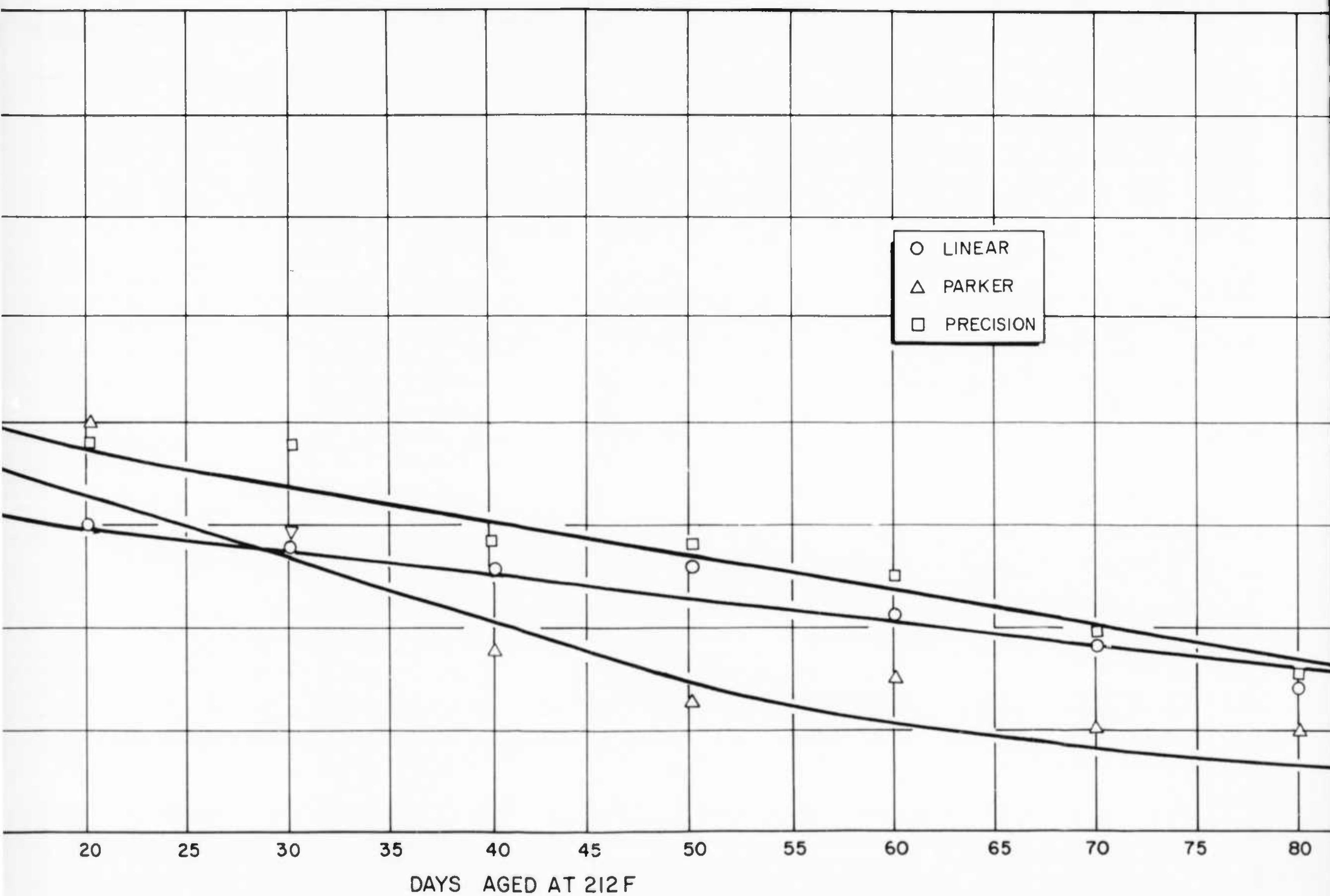
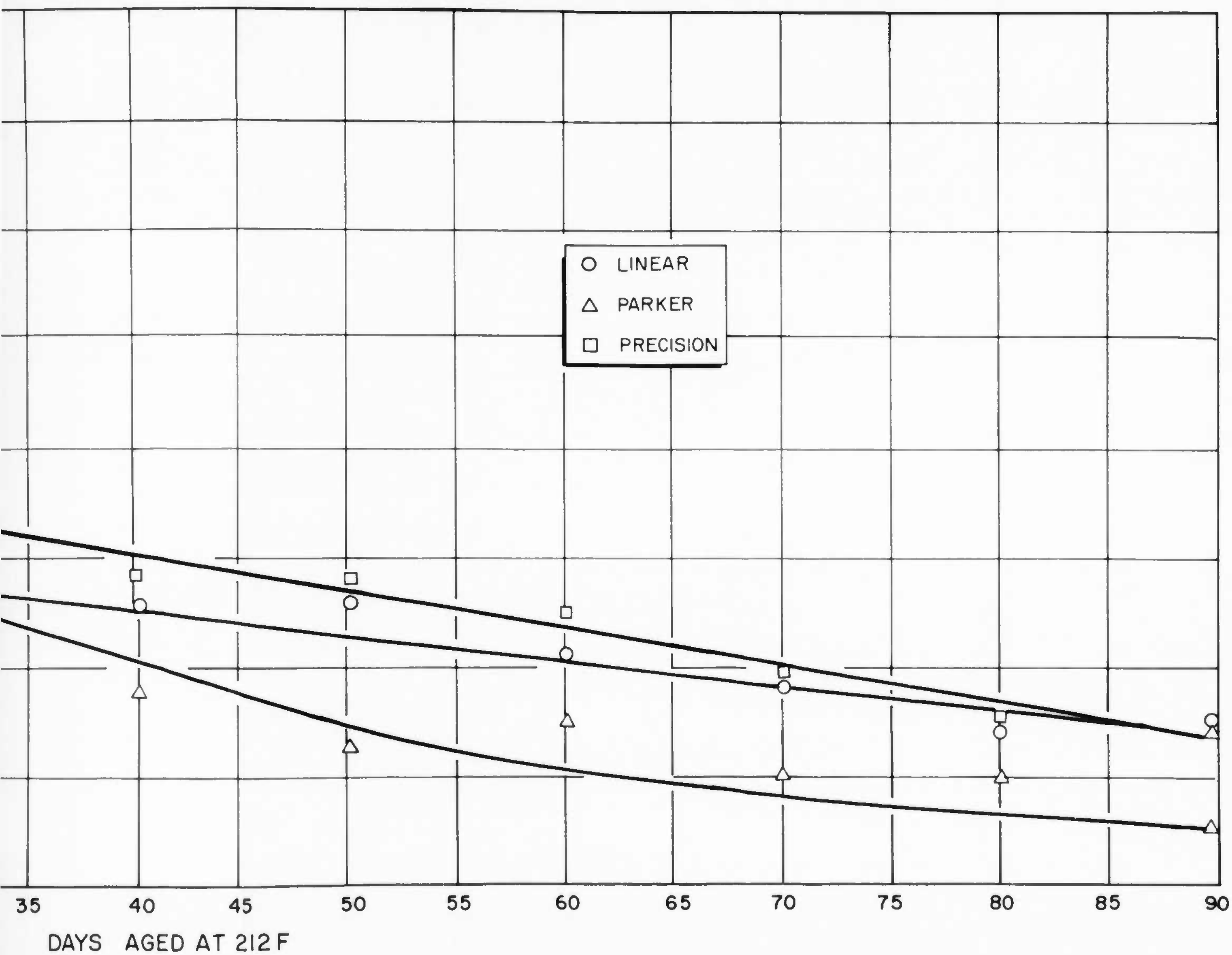


Figure 19. Ultimate E
Aging Time
O-Rings)

2



3

Figure 19. Ultimate Elongation vs Aging Time (MS29513-218 O-Rings)

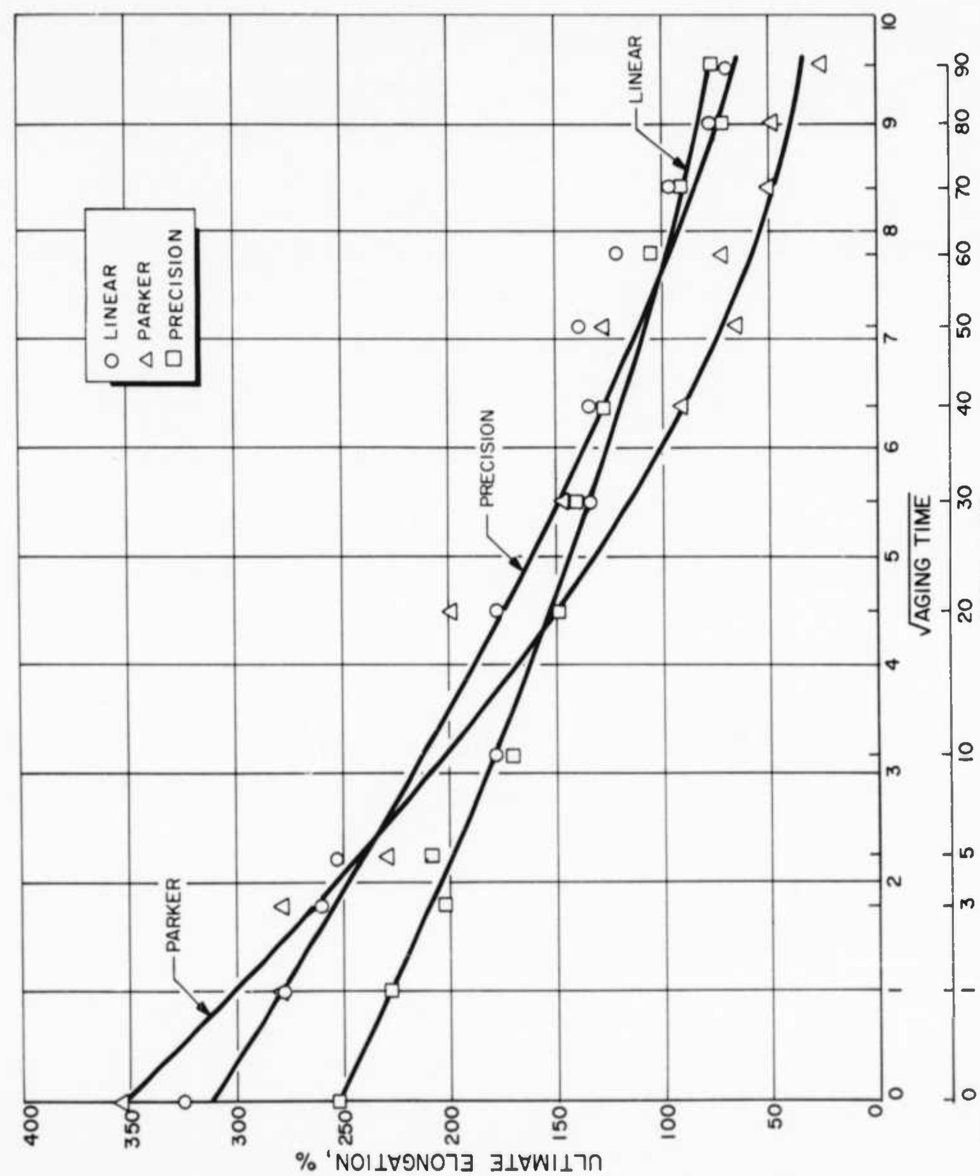


Figure 20. Ultimate Elongation vs $\sqrt{\text{Aging Time}}$

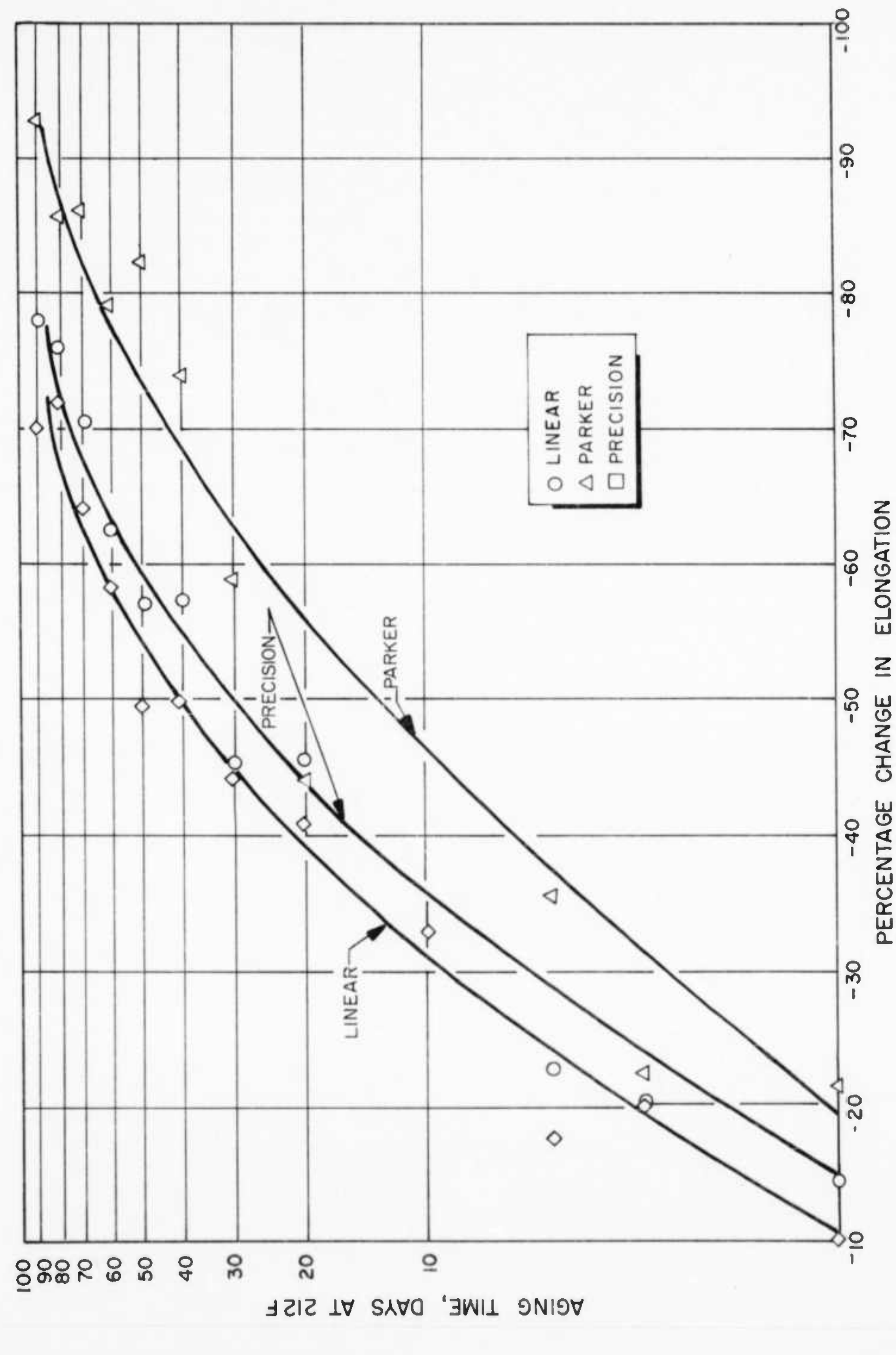


Figure 21 . Aging Time vs Percentage Change in Elongation

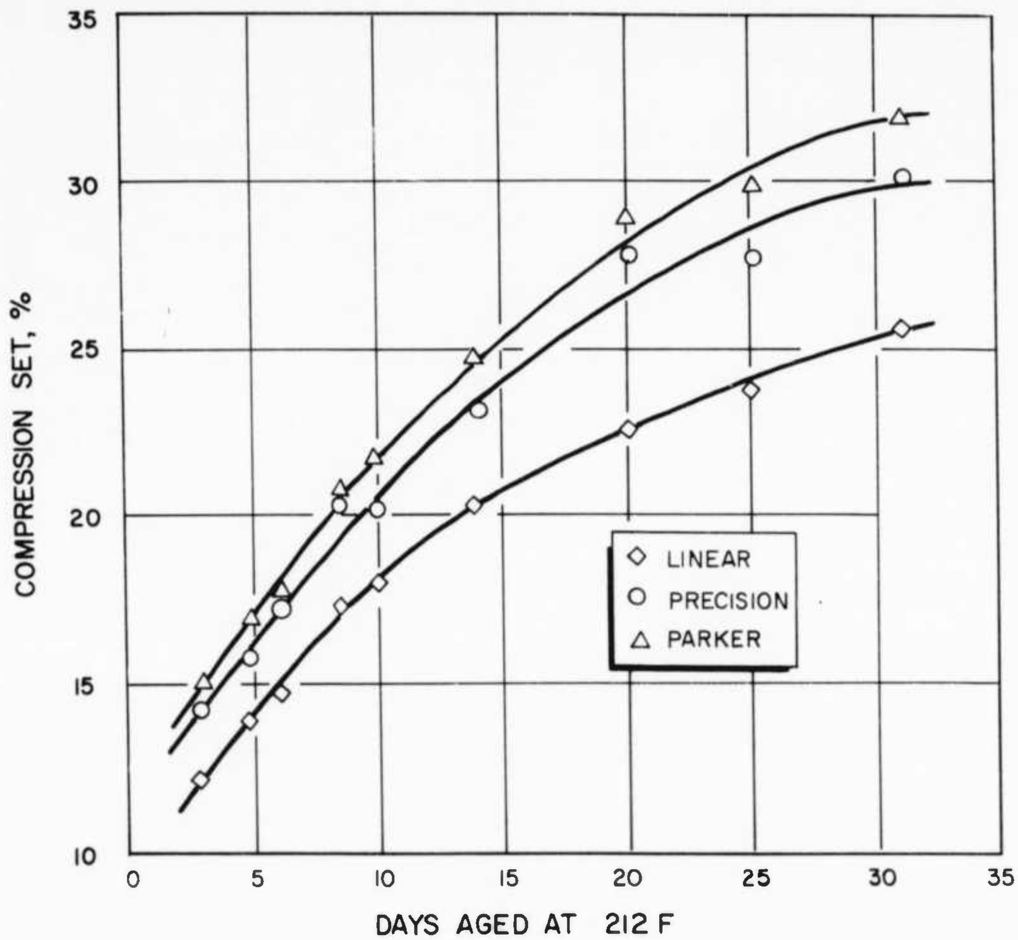


Figure 22 . Compression Set vs Aging Time

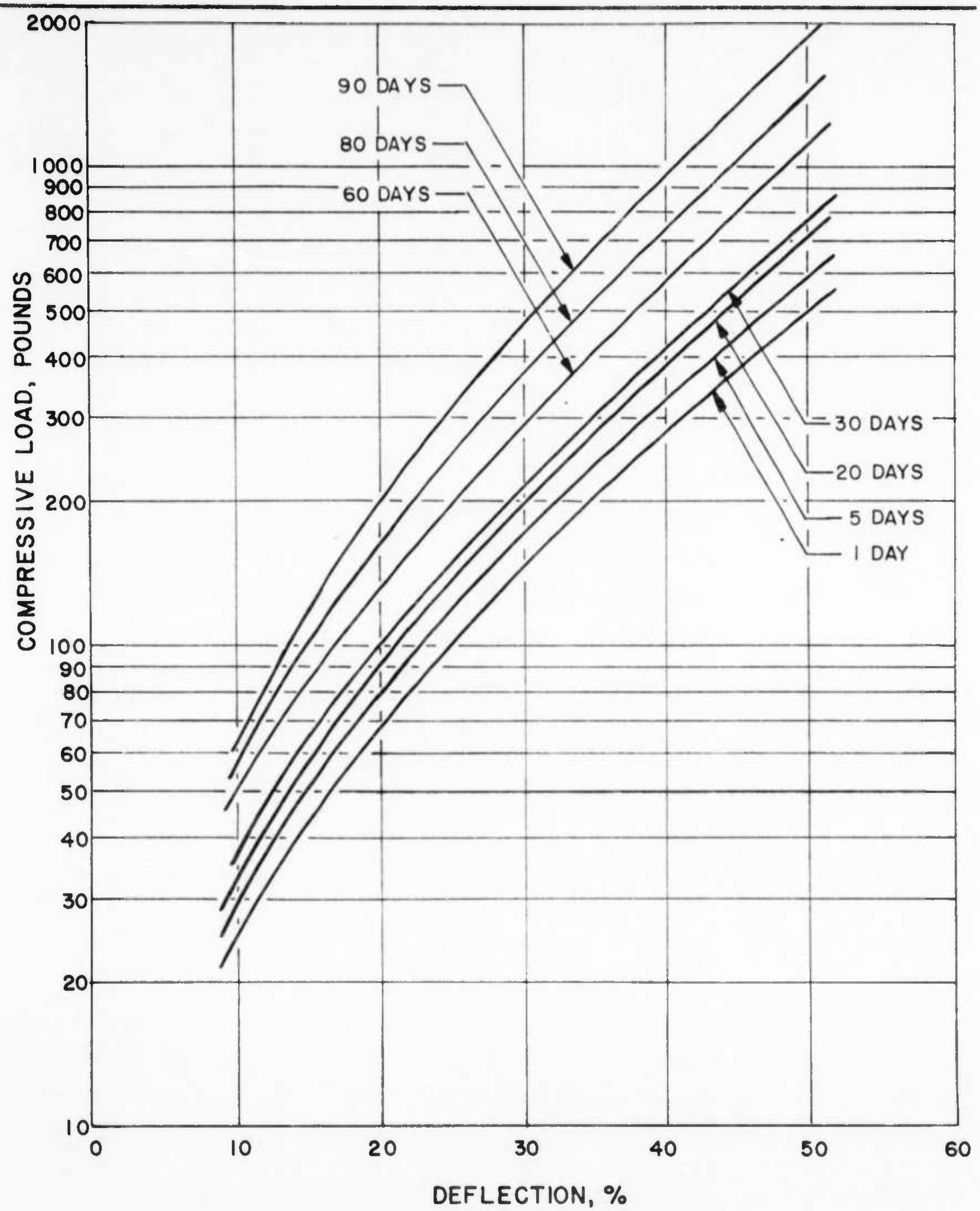


Figure 23. Effect of Aging on Compressive Load-Deflection Characteristics of Linear, Inc., MS29513-218 O-Rings

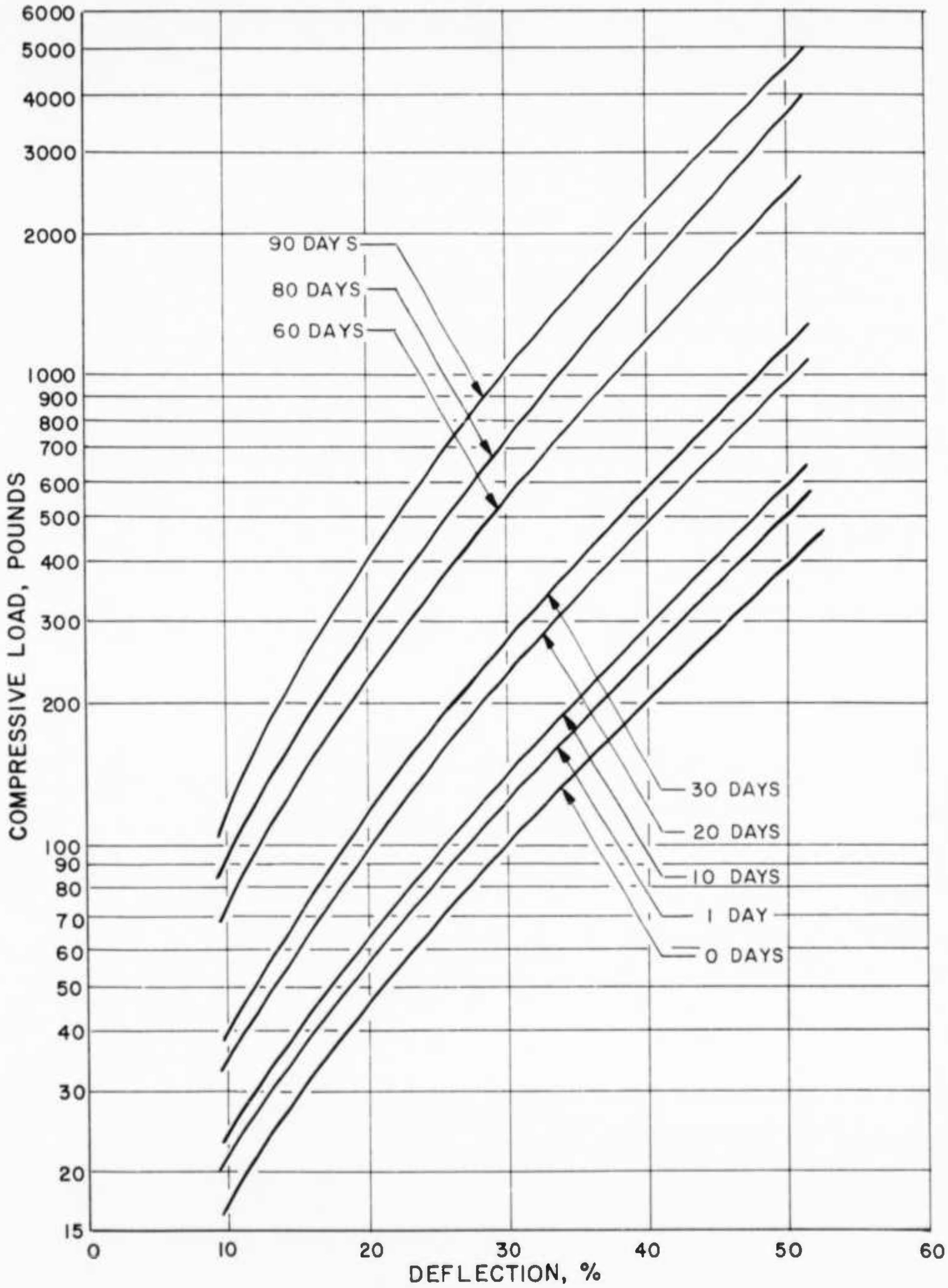


Figure 24 . Effect of Aging on Compressive Load-Deflection Characteristics of Parker Seal Co., MS29513-218 O-Rings

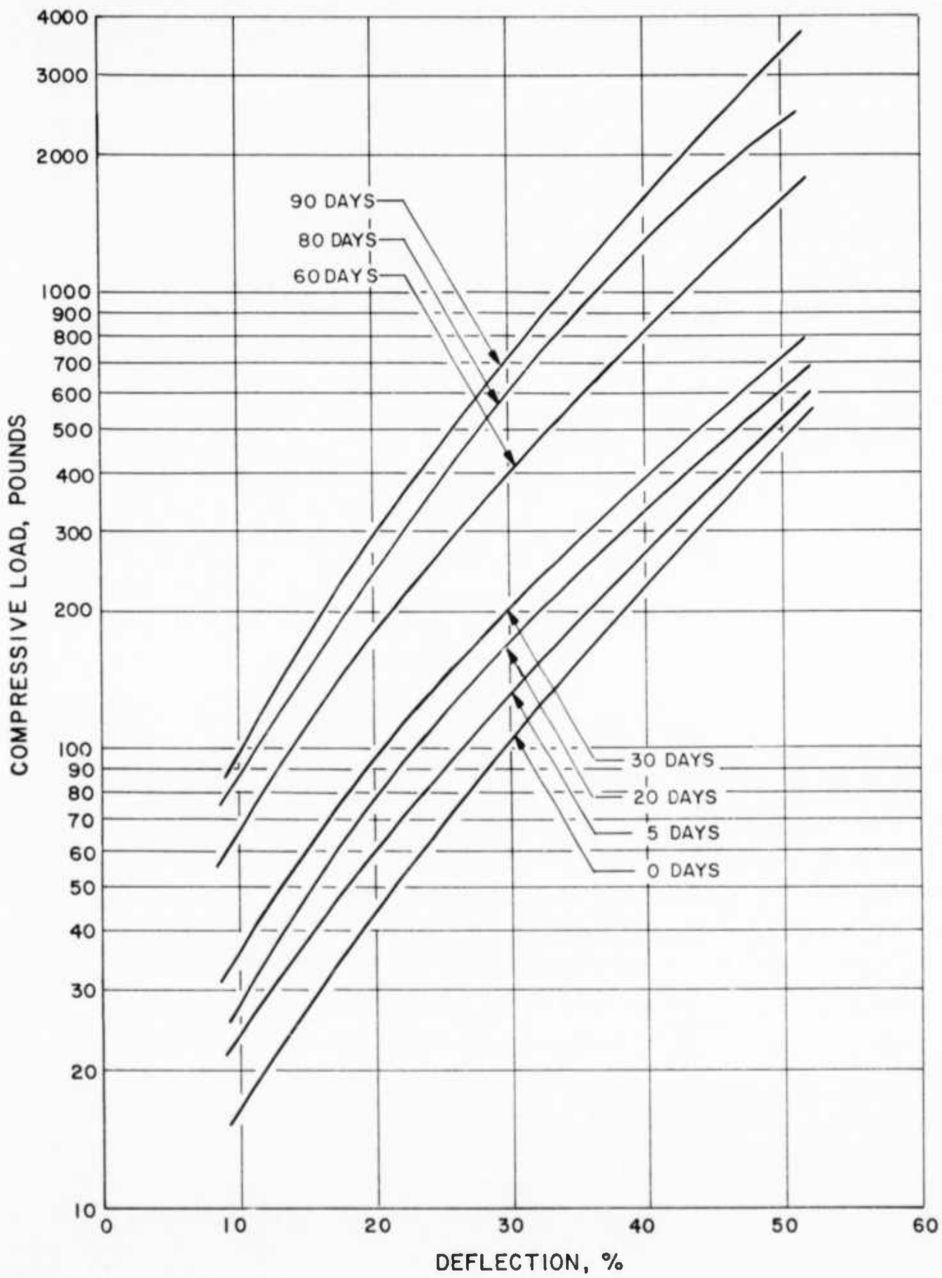


Figure 25. Effect of Aging on Compressive Load-Deflection Characteristics of Precision Rubber Co., MS29513-218 O-Rings

the smallest change occurred with the Linear rings. The usefulness of this dimension is that it provides some indication of the amount of compression set taken by the O-ring when it is in service.

The mathematical models relating this parameter with aging time were not meaningful because the property does not change greatly with age.

HARDNESS

The hardness of an O-ring increases with aging time. The changes in hardness during the initial stages of aging are small and may be masked by the experimental errors involved in making the measurement. Generally, ± 3- to 5-point variations in hardness are common. For detecting large changes in the O-ring caused by aging, hardness is an adequate indicator.

The change in hardness during aging is also a function of the manufacturer. The Linear O-rings harden least (31% increase) in comparison to the Precision (49% increase) and Parker (55%) rings after 90 days of aging at 212 F.

The mathematical models derived for hardness describe adequately the behavior of the O-ring during aging. Good correlations were obtained for the data from Linear and Precision rings fitted to a model of the following type: $H = a + bt + c\sqrt{t}$. The data for Parker were not tested to a model incorporating a $\sqrt{t}$ function. The Parker rings were found to fit the model $H = a + bt + ct^4 + dt^5$.

TENSILE PROPERTIES

Tensile strength values are erratic (although they generally increase with aging time) and exhibit lower percentage changes from the control values than any of the other properties measured. This observation, together with the inherent problems in comparing aged in-service O-rings with new control O-rings and in having a permissible ±15% variation from the military specification qualification of "as determined," indicates that tensile strength is not a sensitive property in evaluating aging of O-rings.

The use of this test in past soft goods analyses at Rocketdyne was based upon its use by the rubber industry and by recognized "experts" as the only standard property test in rubber aging studies. Although the data accumulated by Rocketdyne are not made more useful by them, these other data can be applied when combined with reasonable caution, knowledge of the rocket engine system, data on functional checkouts of the various components containing O-rings during the overhaul programs, and other physical property data and visual examinations of the O-rings.

The decreasing tensile strength of the Parker O-rings after 60 days at 212 F may indicate that the aging process in these rings had reached the point where disaggravative processes occurred and chain scission predominated over crosslinking reactions. The Linear and Precision rings were still under the influence of aggravative reactions and were still increasing in tensile strength at the end of the test period. Attempts to fit polynominal and square-root functions to the data were not successful. The resulting models did not describe the data adequately.

Elongation and tensile stress are definitely sensitive to the aging process. They change significantly and fairly consistently with age. The elongation decreases with age, where the tensile stress increases with age. Tensile stress appears to be the more useful of the two properties in relation to sensitivity, because the changes due to aging are quite large.

The elongation at which the tensile load should be measured should be selected to be about 50% of the ultimate elongation. As the elongation selected approaches the ultimate elongation, the tensile stress results would tend to become more erratic. Again, the rings from Linear exhibited the best aging resistance of the three manufacturers evaluated. Linear rings retained 30% of their original elongation after 90 days aging at 212 F, compared to 22% for Precision rings and only 7% for Parker rings. After 50 days of aging, Linear rings increased in 50% tensile stress by 164% compared to 394% for Precision rings and 684% for Parker rings.

The best mathematical models derived for elongation were of the following type: $E = a + b\sqrt{t}$. A fit of the Parker O-ring data to this equation was not attempted. The models for 50% tensile stress were not particularly adequate in relating this parameter to any of the time functions attempted.

COMPRESSIVE PROPERTIES

The compressive stress of O-rings increases with aging. Thus, a ring requires a higher unit loading after aging to compress it to a fixed percentage than was required before aging. Compressive stress data for each of the three manufacturers are given in Fig. 23 through 25 .

The compressive stress data indicate that the property is generally sensitive to aging, but that it is better suited to detecting gross changes in the material due to aging than to establishing a precise aging period, because in several aging ranges there are only small changes resulting from a change in aging period. Also, the precision of the test values is not particularly good, and the test method would have to be improved to yield less scattered data before any sophisticated analysis could be accomplished. The usefulness of including this property in aging studies is that it is an important parameter in the O-ring sealing mechanism.

The percentage changes in compressive stress after aging are consistently lower for rings from Linear than for those from Parker or Precision. Meaningful relationships were obtained with some success between 10% compressive stress and an aging time function. In addition, interesting results were observed in attempts to correlate this property with other physical property parameters.

The compressive stress is related to 50% tensile modulus and tensile strength, a significant fact because of the possibility of testing a sample for tensile properties and being able to obtain a compressive property merely by manipulation of a mathematical equation. Good correlations of the log (10% compressive stress) with aging time were found for all three manufacturer's rings.

Compression-set values increase consistently with age but, as with compressive stress values, compression-set tests are generally not precise enough to detect subtle aging changes. However, the property is sensitive enough to provide a gross indication of the aging of O-rings. The data presented in Fig. 22 reflect the fact that the Linear rings have lower compression-set values than those from Parker and Precision.

The compression relaxation data indicate that the stress decay of an O-ring changes with time; the load decay decreases as the aging time increases. As with the other compressive properties, these data show an over-all aging phenomenon, but do not particularly demonstrate change from one aging period to the next.

The stress relaxation slopes were calculated using a procedure similar to that used by Trepus et al. (Ref. 18). The trend of the slope values for both Parker and Precision rings is to more negative values, where Linear rings produce fluctuating data (the slope first decreases, then increases).

The Hodgson and Macleish approach, in which stress relaxation data are applied to aging studies, is given in Ref. 23 . A 2-minute tensile relaxation test (performing a tensile relaxation test and reporting the ratio of the initial stress to the stress retained after 2 minutes of relaxation) was applied to aging tests; it was determined that this test is sensitive to aging and, as such, may aid investigators searching for a good, fast, reliable, and sensitive aging test.

An attempt to apply the compressive relaxation data from this study to the procedure and method of calculation in Ref. 23 showed no simple relationships between the aging of nitrile rubber and a 2-minute tensile relaxation test. These data are given in Table 20 .

The test values were plotted vs aging time and vs the square root and logarithmic functions of time. Also, a semilogarithmic plot of aging time vs test value was attempted. No correlation was obtained from any of these plots.

TABLE 20

TWO-MINUTE TENSILE RELAXATION TEST RESULTS

Supplier	Zero Load/Load at Zero Plus 2 Minutes								
	Aging Time, Days								
	0	1	3	5	10	20	30	40	50
Linear	1.039	1.0203	1.0333	1.04233	1.03125	1.0242	1.0628	1.0419	1.0457
	1.055	1.0281	1.0275	1.03211	1.01141	1.0290	1.0421	1.0428	1.0421
	1.044	1.0493	1.0422	1.02112	---	1.0262	1.0473	1.0412	1.0495
Average	1.0460	1.0325	1.0343	1.03185	1.02133	1.0264	1.0507	1.0419	1.0457
Parker	1.0864	1.0695	1.0621	1.08433	1.08750	1.0710	1.1228	1.1286	1.1358
	1.063	1.0718	1.0547	1.09030	1.06919	1.0797	1.0759	1.1225	1.1260
	1.0692	1.0711	1.0767	1.08384	---	---	1.1030	---	1.1255
Average	1.0728	1.0708	1.0645	1.08615	1.07834	1.0753	1.1005	1.1256	1.1291
Precision	1.031	1.0381	1.0273	1.05376	1.03904	1.0517	1.0815	1.0983	1.1069
	1.049	1.0632	1.0557	1.05210	1.02745	1.0695	1.0788	1.1055	1.1042
	1.041	1.0565	1.0705	1.05731	---	1.0592	1.1073	1.1067	1.1303
Average	1.040	1.0526	1.0511	1.05439	1.03324	1.0601	1.0892	1.1035	1.1138

Hodgson and Macleish confined their work to tensile relaxation studies, short-term aging of the materials, use of dumbell samples, and materials other than nitrile rubber. Also, they reported that their work on SBR rubber (this material most closely resembled nitrile rubber of all the materials they evaluated) indicated that no apparent correlation existed between the R-2 type of aging test and SBR rubber.

CORRELATION OF TENSILE BREAKS WITH O-RING IDENTIFICATION MARKINGS

The locations of the tensile failures in the O-rings were observed in relation to the color-coding system which provides specification and manufacturer identification. Recent changes in some military O-ring specifications have eliminated the color-code system, based upon the belief that the area of the O-ring having the color-coding is the weakest part of the ring, and that ultimately the failure of the ring will be at this point. No failure occurred in color-coded areas during the test program. Breaks during the ultimate elongation tests occurred randomly around the circumference of the ring.

SUMMARY

O-rings from different manufacturers show definite differences in aging rate. The color-coding system for identification of suppliers should be maintained for purposes of quality control and if future studies of in-service soft goods are to be meaningful. Those rings made to specifications which do not call for manufacturer designation codes should use the color-coding system. Of the properties evaluated, tensile stress, elongation, and compressive stress appear to be the most sensitive to detecting changes in the material due to aging. Tensile stress is the most sensitive of these three properties.

TASK 4--CORRELATION OF ACCELERATED AGING WITH NATURAL AGING

The aging of elastomers under widely different conditions of use was investigated, and considerable effort has been devoted to the design of accelerated aging tests. One general conclusion is that no rapid aging method can be expected to do more than approximate the reaction of the elastomer to its service environment. The principal reason for this is that more than one reaction occurs during aging, and one reaction may be more dependent on temperature, oxygen pressure, or some other aging factor, than another. No correlation between accelerated aging tests and product performance can be expected if the ultimate failure of the elastomer is due to conditions unrelated to the oxidative changes occurring in the laboratory test. Failures because of flex cracking, ozone cracking, light catalyzed oxidation, and fatigue would not be expected to correlate with the results of the standard laboratory accelerated aging tests. Furthermore, in the particular case of O-ring sealing, the mechanical and environmental conditions under which a seal must operate have a considerable bearing on the life of the seal.

The objective of this phase of the O-ring aging study program has been to obtain a correlation between natural (in-service) and accelerated aging of O-rings. In particular, the accelerated aging data (at 212 F) from the Task 3 tests on the MIL-P-5315 O-ring compounds supplied by Linear, Inc., the Parker Seal Company, and Precision Rubber were utilized.

SELECTION OF ACCELERATED AGING CONDITIONS

Aging Methods

A variety of accelerated aging tests is available, the objectives of which are to predict in a short-time test what will occur to an elastomer in a longer time under natural conditions. The standard methods for studying aging (particularly oxidative degradation) are outlined in the following paragraphs.

Oven-Aging Test (ASTM D573-53). This test utilizes a circulating air-oven maintained at a desired temperature which is generally 158 F. Samples are exposed for various time intervals, e.g., 7, 14, and 28 days, then tested for their stress-strain properties, and the deterioration from unaged samples is noted. Temperatures higher than 158 F are necessary for many of the synthetic elastomers. Rock Island Arsenal (Ref. 3) has found that 158 F is too low a temperature to produce any appreciable aging in a short-time period for nitrile rubber. Fairly good correlations between the changes which take place in oven aging tests and those which occur at room temperatures have been found (Ref. 15 , 25 , 26 , and 27). However, no constant factor can be applied because different materials respond differently to a change of temperature. This method may produce erroneous results if very dissimilar elastomers are aged together.

Test-Tube Method (ASTM D865-57). The test-tube method of aging involves suspending samples in large test tubes (or suitable containers) which are heated by immersion in an oil bath or aluminum block heater. Air circulation is by convection through a pair of tubes inserted through the stoppers. The particular advantages of this method are that:

1. The specimens of each materials are isolated from other materials being aged so that contamination of one material by volatile products from another is eliminated.
2. The use of an aluminum block heater (or oil bath) as the source of heat permits good control of temperature.
3. The air circulation (by convection) is moderate and constant for a particular exposure temperature and permits steady, constant aging exposure.

Air Bomb Test (ASTM D454-53). The air-pressure heat test subjects samples to a relatively high temperature, 260 F, and air pressure at 80 psi and was intended originally to provide a set of conditions somewhat like those prevailing in inner tube service.

Oxygen Bomb Test (ASTM D572-61). The oxygen bomb method utilizes a pressure vessel capable of handling oxygen at 300 psi pressure and 158 F. This is essentially a device for increasing the rate of reaction by increasing the oxygen concentration. As a result, the time intervals of exposure are generally shorter than for the oven test, e.g., 1, 2, and 7 days. The effects produced are also reduced compared to those resulting from oven-aging.

Selection of Oven Aging Method

Of the standard methods of aging elastomers, test tube and oven aging are probably two of the best techniques available. Test tube aging, or some form of it, is perhaps the best choice when testing widely different elastomeric compounds. However, the use of this procedure in a program such as this O-ring aging program, in which hundreds of O-rings were to be aged, would be quite cumbersome. Furthermore, the principal advantage of the test tube method over the oven method of aging (the elimination of contamination of one material by volatile products from another when different materials are being aged) is negated since similar formulations of the same basic elastomer system are involved in the aging program.

The oven aging technique is still the most widely used method of aging elastomers. It permits the simple, efficient, and effective aging of hundreds of O-ring samples. The method has been successfully used in many aging studies. Rocketdyne has used the oven-aging method in this program.

Selection of Aging Temperature

Although aging tests are often run at 158 F, Rocketdyne selected 212 F as the aging temperature. The reason for accelerated aging is to speed up the normal anticipated changes in the material which will occur with time. The 158 F temperature has been reported (Ref. 3) to be too low to effect any appreciable aging in a relatively short period of time. Very high temperatures are unrealistic in that although they drastically accelerate the aging, they also promote reactions which are not representatives of the type and nature of aging at ordinary operating temperatures and/or change the reaction rates of normal aging reactions. A temperature of 212 F appears to be a reasonable compromise by providing an effective acceleration of aging while still producing no drastically different types of aging reactions and mechanisms from those that occur at normal service conditions which is basically room temperature (Ref. 28).

TESTING OF AGED O-RINGS

The details of the testing of the accelerated aged O-rings are described in the report section for Task 3 of this over-all program. Included in the section are discussions of the samples used, properties tested, the test procedures, and test results. The data are reported in Tables 16, 17, and 18 and Fig. 14 through 25.

ACCELERATED--NATURAL AGING CORRELATION

To evaluate the usefulness and applicability of the information obtained in Task 3, attempts were made to obtain correlations between the accelerated aging (at 212 F) and the natural (in-service) aging of O-rings.

However, in evaluating the natural (in-service) aging data, from past soft goods studies (Ref. 2), it becomes apparent that other than observing random inconsistancies in the data, there are no significant changes in properties (W-diameter, hardness, and tensile strength) as a result of in-service life. Furthermore, sufficient data has not been compiled on either the 100% tensile stress (tensile modulus) or compressive stress (compression-deflection) to formulate any correlations based on these properties. Thus, it is meaningless to compare the accelerated aging data with in-service data.

While a substantial amount of information has been published on the natural aging of nitrile rubber compounds, such data are not directly applicable or meaningful for correlation purposes with a specific nitrile formulation, such as the specific O-ring compounds included in this aging program. If any realistic and useful correlation is to be achieved, it must be between natural and accelerated aging of the same compound.

Fortunately, data on the aging of MIL-P-5315 rings are available from a Rubber Manufacturers Association (RMA) study project (Ref. 29) which investigated the change in physical properties of the compounds from different manufacturers qualified to this particular military specification with shelf aging time. The data available are for the 100% tensile stress and ultimate elongation of Parker Seal Company's MIL-P-5315 compound and for the tensile strength and elongation of Precision Rubber's compound qualified to the same military O-ring specification. Similar information for the Linear, Inc., compound was not available.

Thus, because of the apparently low degree of deterioration of rocket engine in-service O-rings and the unavailability of other natural (in-service type) aging information about the specific nitrile rubber compounds included in the accelerated aging program, the basis for the natural aging data with which to compare the accelerated aging data is the shelf-aging data of RMA.

Both shelf and accelerated aging data are plotted in Fig. 26 and 27. By plotting both sets of data on the same graph (using different scaling factors), curves were obtained from which some interesting correlations were made.

However, these correlations can only approximate the actual situation. Several factors are responsible for this limitation. First, the wide scattering of the natural (shelf) aging data tends to make the soundness of the curve fit doubtful. Furthermore, the data represent an average of test values obtained on an unknown number of samples. The range of these values, because of the acknowledged problems and difficulties in obtaining precise physical property values, may be appreciable and may, if considered and plotted, require the redrawing of the aging curve upon which the correlations have been based.

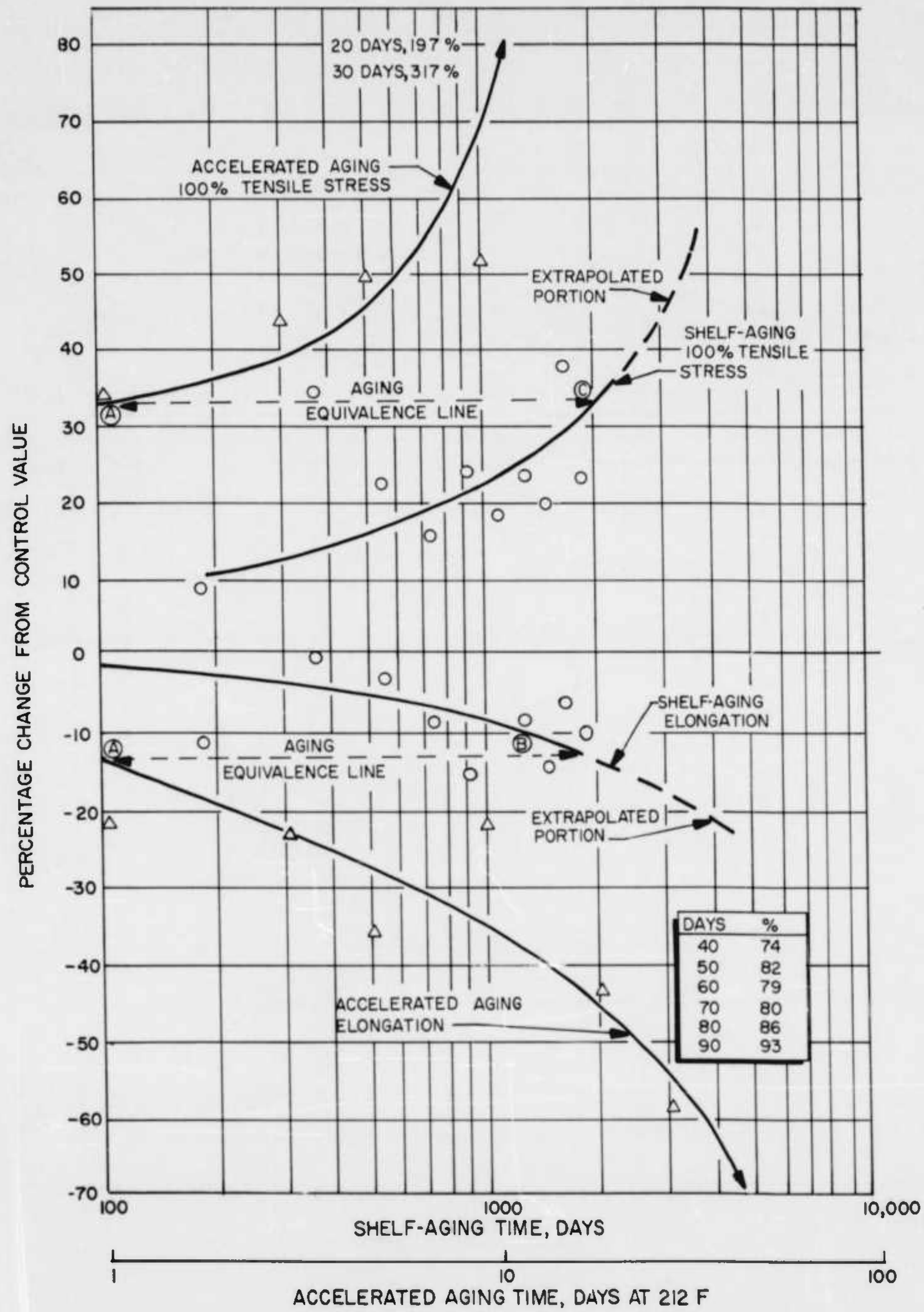


Figure 26. Percentage Change in Physical Properties vs Shelf Aging and Accelerated Aging (Parker Compound MIL-P-5315)

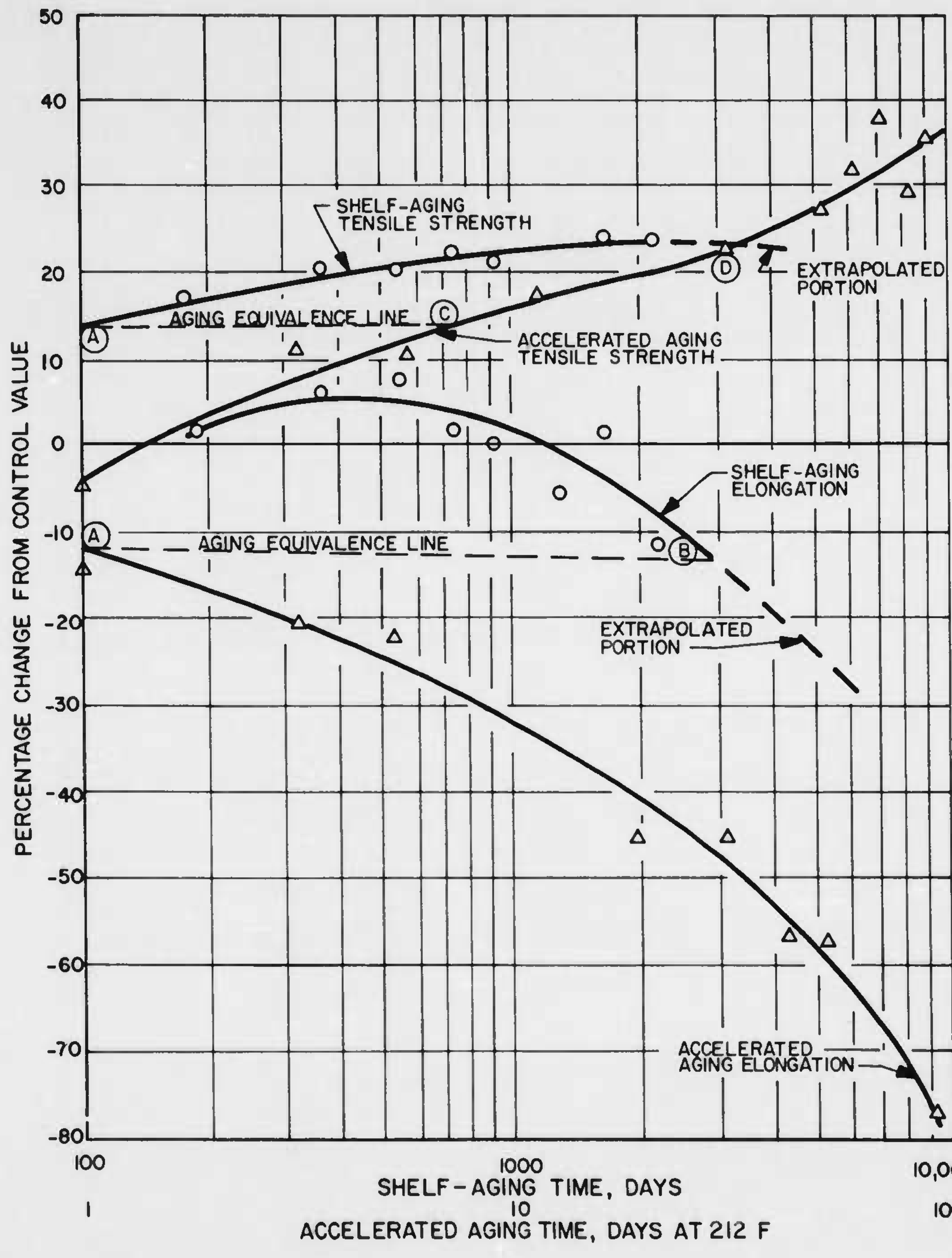


Figure 27. Percentage Change in Physical Properties vs Shelf Aging and Accelerated Aging (Precision Compound MIL-P-5315)

Secondly, because of the limited shelf-aging property data, it was necessary to extrapolate the curve, which has been fitted to measured values, to longer aging times. If a change in aging rate and a corresponding change in curve configuration occurs, then the value of the correlations obtained is greatly reduced.

It appears that for both Parker Seal Company and Precision Rubber compounds there is some correlation between the two sets of elongation data. In Fig. 26, it may be seen that although the initial curve for the elongation of shelf-aged rings is different from that for the accelerated data, once point B on the dotted horizontal aging equivalence line is reached (at approximately 1900 days of shelf aging), the shape of the curve is similar to that for the accelerated-aging data.

This suggests that 1 day of accelerated aging of this compound at 212 F produces the same percentage change (from the control value) in the property as approximately 1900 days of shelf aging. After this period of time, the shape of the two aging curves is very similar and this indicates that the rate of the change of elongation with time is similar. The correlation of the 100% tensile stress data also indicate some similarity in aging rates between shelf- and accelerated-aged material.

The aging equivalence line (line AC) for these curves relates 1 day of 212 F accelerated aging to approximately 2000 days shelf aging. This compares favorably with a 1:1900 ratio for the elongation data. It is encouraging to find the two physical properties having similar aging equivalence relations.

Meaningful correlations for the data on Precision Rubber's MIL-P-5315A compound (Fig. 27) were not achieved.

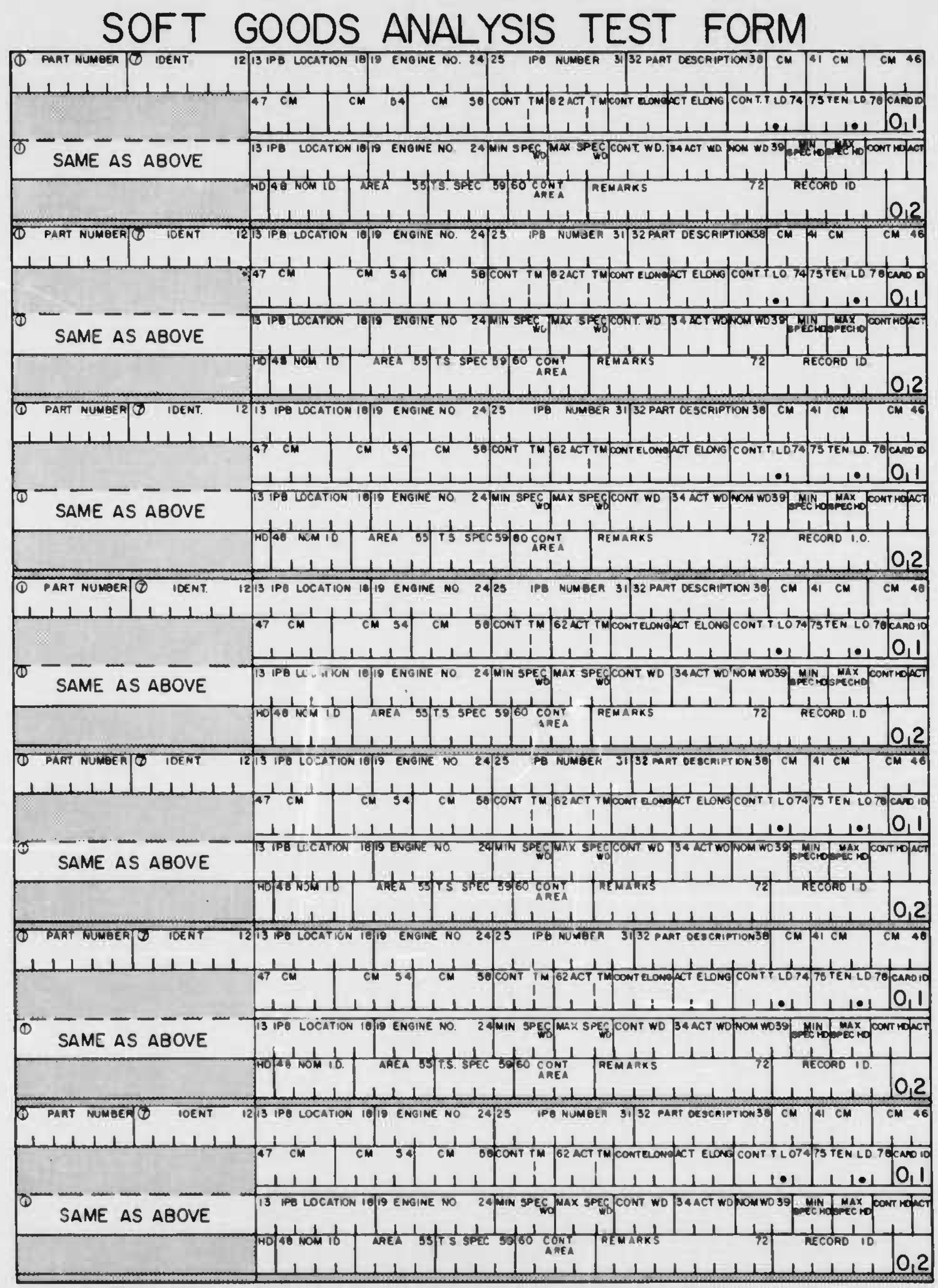
No correlation at all is possible for tensile strength because of the two aging curves. The shelf-aged elongation curve after point B on the equivalence line may follow a similar curve as that for the accelerated aging curve. However, due to the unusual nature of the shelf-aging curve (the initial rise in elongation with time), the reliability of this curve is doubtful. Although the usefulness of the aging equivalence ratio (days accelerated aging at 212 F shelf-aging time) in this case is in doubt because of the problems of curve fitting, it is not unusual to find that any one accelerated aging technique does not predict accurately all of the physical changes that will occur during natural long-term service and storage.

TASK 5--THE MATHEMATICAL APPROACH TO THE ANALYSIS OF O-RING AGING DATA

To improve the techniques and procedures used in aging studies of O-rings, Rocketdyne has been utilizing the most modern mathematical tools available. Information retrieval and calculation programs have been prepared and used and are being improved constantly. Data accumulated from soft goods analyses have been recorded and stored on magnetic computer tape, and data from analyses made previous to the inception of computer programs in soft goods study will be transferred to the magnetic computer tape for permanent retention and comparison. The computer in use is Rocketdyne's IBM 7090. The present means of recording the data and of presenting it to the computer is shown in Fig. 28 and 29. Basically, the program provides an historical data retrieval system for analyzing and comparing the properties of O-rings removed from overhauled engine systems.

In conjunction with this system, a program has been written which enables Rocketdyne personnel to simply feed the computer raw data obtained in laboratory testing of soft goods, and obtain calculated physical property values. For example, the tensile load (pounds) is converted into tensile strength (psi), and the compressive-deflection load (pounds) is converted to load per inch of circumference (lb/in.).

It is anticipated that this computer program for storage and analysis of data resulting from soft goods evaluations will materially lessen the length of time and amount of work involved in these evaluations, and will permit Rocketdyne personnel to more thoroughly determine the extent of



TEST FORM FROM 11-1-62 THROUGH 1-1-63

Figure 28. Soft Goods Analysis Test Form

SOFT GOODS ANALYSIS TEST FORM

NON O-RING COMPONENTS

1	3 PART ID 14	15 PART LOC. 20	21 IPB LOC. 26	27 ENG. NO. 32	33 IPB NO. 39	40 PART DESCRIPTION 46
	47 HD	48 COMMENTS				CARD ID 03
1	3 PART ID 14	15 PART LOC. 20	21 IPB LOC. 26	27 ENG. NO. 32	33 IPB NO. 39	40 PART DESCRIPTION 46
	47 HD	48 COMMENTS				CARD ID 03
1	3 PART ID 14	15 PART LOC. 20	21 IPB LOC. 26	27 ENG. NO. 32	33 IPB NO. 39	40 PART DESCRIPTION 46
	47 HD	48 COMMENTS				CARD ID 03
1	3 PART ID 14	15 PART LOC. 20	21 IPB LOC. 26	27 ENG. NO. 32	33 IPB NO. 39	40 PART DESCRIPTION 46
	47 HD	48 COMMENTS				CARD ID 03
1	3 PART ID 14	15 PART LOC. 20	21 IPB LOC. 26	27 ENG. NO. 32	33 IPB NO. 39	40 PART DESCRIPTION 46
	47 HD	48 COMMENTS				CARD ID 03
1	3 PART ID 14	15 PART LOC. 20	21 IPB LOC. 26	27 ENG. NO. 32	33 IPB NO. 39	40 PART DESCRIPTION 46
	47 HD	48 COMMENTS				CARD ID 03
1	3 PART ID 14	15 PART LOC. 20	21 IPB LOC. 26	27 ENG. NO. 32	33 IPB NO. 39	40 PART DESCRIPTION
	47 HD	48 COMMENTS				CARD ID 03
1	3 PART ID 14	15 PART LOC. 20	21 IPB LOC. 26	27 ENG. NO. 32	33 IPB NO. 39	40 PART DESCRIPTION 46
	47 HD	48 COMMENTS				CARD ID 03
1	3 PART ID 14	15 PART LOC. 20	21 IPB LOC. 26	27 ENG. NO. 32	33 IPB NO. 39	40 PART DESCRIPTION 46
	47 HD	48 COMMENTS				CARD ID 03
1	3 PART ID 14	15 PART LOC. 20	21 IPB LOC. 26	27 ENG. NO. 32	33 IPB NO. 39	40 PART DESCRIPTION 46
	47 HD	48 COMMENTS				CARD ID 03
1	3 PART ID 14	15 PART LOC. 20	21 IPB LOC. 26	27 ENG. NO. 32	33 IPB NO. 39	40 PART DESCRIPTION 46
	47 HD	48 COMMENTS				CARD ID 03
1	3 PART ID 14	15 PART LOC. 20	21 IPB LOC. 26	27 ENG. NO. 32	33 IPB NO. 39	40 PART DESCRIPTION 46
	47 HD	48 COMMENTS				CARD ID 03
1	3 PART ID 14	15 PART LOC. 20	21 IPB LOC. 26	27 ENG. NO. 32	33 IPB NO. 39	40 PART DESCRIPTION 46
	47 HD	48 COMMENTS				CARD ID 03
1	3 PART ID 14	15 PART LOC. 20	21 IPB LOC. 26	27 ENG. NO. 32	33 IPB NO. 39	40 PART DESCRIPTION 46
	47 HD	48 COMMENTS				CARD ID 03

Figure 29. Soft Goods Analysis Test Form
(Non O-ring Components)

the aging of soft goods. However, to gain the benefits of a machine analysis, standardized nomenclature must be used so that the correct data can be entered on the Soft Goods Analysis Test Forms (Fig. 28 and 29).

Thus, the following method is suggested for identification procedures during engine overhaul and subsequent soft goods evaluations:

1. A card or tag shall be attached to each individual part or group of identical parts from one location, showing the following:

   a. Engine serial number

   b. Component in which the part is placed; the following component locations only shall be used and may be abbreviated as shown:

	Location	Abbreviation
(1)	Major Components System	MCS
(2)	Pneumatic Control System	PCS
(3)	Lubrication System	LS
(4)	Gas Generator System	GGS
(5)	Start System	SS
(6)	Hydraulic System	HS
(7)	Propellant Feed System	PFS
(8)	Exhaust System	ES

   c. IPB Number: Illustrated Parts Breakdown used in identifying the part

d. IPB Location: The figure number and index number where the part appears in the applicable Illustrated Parts Breakdown

c. Part Number: AN or MS number of the part removed for test

This identification procedure will considerably shorten laboratory and engineering time in the analysis.

Included in Appendix F are the actual instructions directed to technicians to enable them to accurately and effectively record data which then would be transferred to keypunch IBM cards and, finally, to IBM magnetic tape. These instructions also provide a description of the soft goods analysis program.

After receiving the raw data, the computer performs all the numerical calculations, compares the final values to the limits set by specification, and displays the information derived in tabular or graphical form for easy analysis. Examples of the various reports are shown in Table 21 through 23 and Fig. 30 and 31.

Table 21 shows one page of the general tabulation of O-rings. Table 22 includes the tabulation of non O-ring components. The tabulations are arranged by component in which the parts are found. Table 23 presents a tabulation of soft goods that showed test results outside of specification limitations. Figure 30 and 31 show computer plots of compressive load in pounds per mean inch of circumference vs percentage deflection. The rapid dropoff of the graph in Fig. 31 indicates that no value was recorded for compressive modulus at 60% deflection--not that the compressive modulus at 60% deflection was zero.

TABLE 21

RESULTS OF TESTS ON O-RINGS FROM PROPELLANT FEED SYSTEM

PART NUMBER	IPB LOCATION	W DIAMETER, INCHES SPEC MIN VAL	SPEC MAX VAL	CON-TROL VAL	ACT VAL	SHORE-A HARDNESS SPEC MIN VAL	SPEC MAX VAL	CON-TROL VAL	ACT VAL	TENSILE STRENGTH, PSI SPEC VAL	CON-TROL VAL	ACT VAL	ELONGATION PERCENT CON-TROL VAL	ACT VAL	100-PERCENT TEN MOD PSI CON-TROL VAL	ACT VAL
~~MS 29512-12~~	~~26-65~~	~~.112~~	~~.120~~	~~.115~~	~~.112~~	~~55~~	~~65~~		~~70~~	~~1350~~	~~1592~~			~~156~~	~~757~~	
			MISPLACED													
MS 29512-12	26-74	.112	.120	.115	.125	55	65		64	1350	1592	792		130	757	604
			DEFORMED													
MS 29513-113	30-7	.100	.106	.100	.099	55	65	60	62	1350	1744	1506		259	628	
~~MS 29513-116~~	~~27-72~~	~~.100~~	~~.106~~	~~.101~~	~~.098~~	~~55~~	~~65~~	~~61~~	~~62~~	~~1350~~	~~1662~~	~~1476~~		~~193~~	~~400~~	
MS 29513-124	27-65	.100	.106	.100	.103	55	65	61	68	135	1897				423	
			GREASY													
MS 29513-242	26-3	.135	.143	.136	.135	55	65	63	65	1350	1545	493		100	359	474
			DIRTY													
~~MS 29513-247~~	~~26-8~~	~~.135~~	~~.143~~	~~.138~~	~~.135~~	~~55~~	~~65~~		~~61~~	~~1350~~	~~1020~~	~~1026~~		~~177~~	~~349~~	
			DIRTY													
MS 29513-247	26-8	.135	.143	.138	.135	55	65		63	1350	1020	1164		204	349	441
			DIRTY													
MS 29513-251	26-22	.135	.143	.137	.127	55	65		64	1350	1565	1757		250	320	
			DIRTY													
~~MS 29513-251~~	~~26-13~~	~~.135~~	~~.143~~	~~.137~~	~~.132~~	~~55~~	~~65~~		~~64~~	~~1350~~	~~1565~~	~~954~~		~~190~~	~~320~~	~~300~~
			DIRTY													
AN 6227 -12	27-44	.100	.106	.103	.136	65	71	66	68	1350	1530	1614		184	627	
AN 6227 -12		.100	.106	.103	.104	65	71	66	70	350	1530	1373		146	627	
~~AN 6227 -12~~	~~27-26~~	~~.100~~	~~.106~~	~~.103~~	~~.105~~	~~65~~	~~71~~	~~66~~	~~66~~	~~1350~~	~~1530~~	~~1450~~		~~130~~	~~627~~	~~1036~~
			GREASY													
AN 6227 -15	28-66	.135	.143	.139	.141	65	71	67	68	1350	1570	1507		115	543	
AN 6227 -18	30-8	.135	.143		.140	65	71		72	1350				135		
~~AN 6227 -33~~	~~26-62~~	~~.205~~	~~.215~~	~~.202~~	~~.211~~	~~65~~	~~71~~	~~65~~	~~74~~	~~1350~~	~~1522~~	~~1344~~		~~110~~	~~616~~	
AN 6227 -45	27-4	.205	.215	.205	.206	65	71	68	77	1350	1758	1671		146	791	
~~AN 6227 -45~~	~~28-4~~	~~.205~~	~~.215~~	~~.205~~	~~.213~~	~~65~~	~~71~~	~~68~~	~~71~~	~~1350~~	~~1758~~	~~1468~~		~~120~~	~~791~~	
			DIRTY													
AN 6230 -6	28-70	.135	.143	.139	.140	63	73	65	68	1350	1490	1632		148	722.	
			GREASY													
AN 6230 -6	27-51	.135	.143	.139	.141	63	73	65	70	1350	1490	1513		155	722	
			GREASY													
~~MS 28778-12~~	~~26-65~~	~~.112~~	~~.120~~	~~.113~~	~~.115~~	~~83~~	~~93~~		~~83~~	~~1485~~	~~1824~~	~~1217~~		~~82~~	~~1775~~	
			DEFORMED													
MS 28778-12	26-65	.112	.120	.113	.124	83	93		82	1485	1824	1557		93	1775	
			DEFORMED													
MS 28778-16	30-2	.112	.120	.113	.110	83	93		84	148	1324				1206	
			DEFORMED													

TABLE 22

RESULTS OF TESTS ON OTHER SOFT GOODS
FROM GAS GENERATOR SYSTEM

PART NUMBER	IPB LOCATION	DESCRIPTION	COMMENTS
8-3054-1PNA	31-78	GASKET	FLEXITALLIC GASKET DIRTY
10-2453-1PNA	31-73	GASKET	FLEXITALLIC GASKET DIRTY
9512-44012	32-13	GASKET	CARBON DEPOSITS
305711-3	33-41	SEAL	
LD2610900204	33-65	GASKET	
9669-44121	33-4	GASKET	
MS28777-4	31-97	RING	DEFORMED
MS28777-8	31-101	RING	DEFORMED
MS28777-8	31-91	RING	DEFORMED

TABLE 23

ELONGATION, TENSILE STRENGTH, AND TENSILE MODULUS DISCREPANCIES,
O-RINGS FROM PROPELLANT FEED SYSTEM

Part Number	IPB Location	Elongation, %		Tensile Strength, psi		100% Tensile Modulus, psi		Comments
		Actual Value	Control Value	Actual Value	Control Value	Actual Value	Control Value	
MS29512-12	26-74	130		792	1592	604	757	Deformed
MS29513-113	30-7	259		1506	1744		628	
MS29513-116	27-72	193		1470	1662		400	
MS29513-242	26-3	100		493	1545	474	359	Dirty
MS29513-251	26-13	190		954	1565	388	320	Dirty
AN6227-12		146		1373	1530		627	
AN6227-12	27-26	130		1458	1530	1036	627	Greasy
AN6227-15	28-66	115		1507	1570		543	
AN6227-33	28-62	110		1344	1522		816	
AN6227-45	27-4	146		1671	1758		791	
AN6227-45	28-4	120		1468	1758		791	Dirty
MS28778-12	26-65	82		1217	1824		1775	Deformed
MS28778-12	26-65	93		1557	1824		1775	Deformed

This computer program has utilized to analyze the soft goods data from Atlas engine S/N 222132 (the results are presented in Rocketdyne Report R-5017).

The necessity for including accurate and precise control values for O-rings in the computer program has prompted a special study by Rocketdyne's Materials and Processes Group to explore the problems associated with obtaining such values. The study was focused particularly upon the determination of the effect on tensile strength values of different O-ring diameters and cross sections, and different load and strain rates. The results of these investigations are reported in Appendix G.

The experience with the present computer program has uncovered some limitations. Accordingly, a more sophisticated program has been developed to incorporate desired changes. The changes from the original program, the reasons for the changes, the anticipated benefits accruing from the changes, and a description of the program is discussed in Rocketdyne Report R-5290 (Ref. 30).

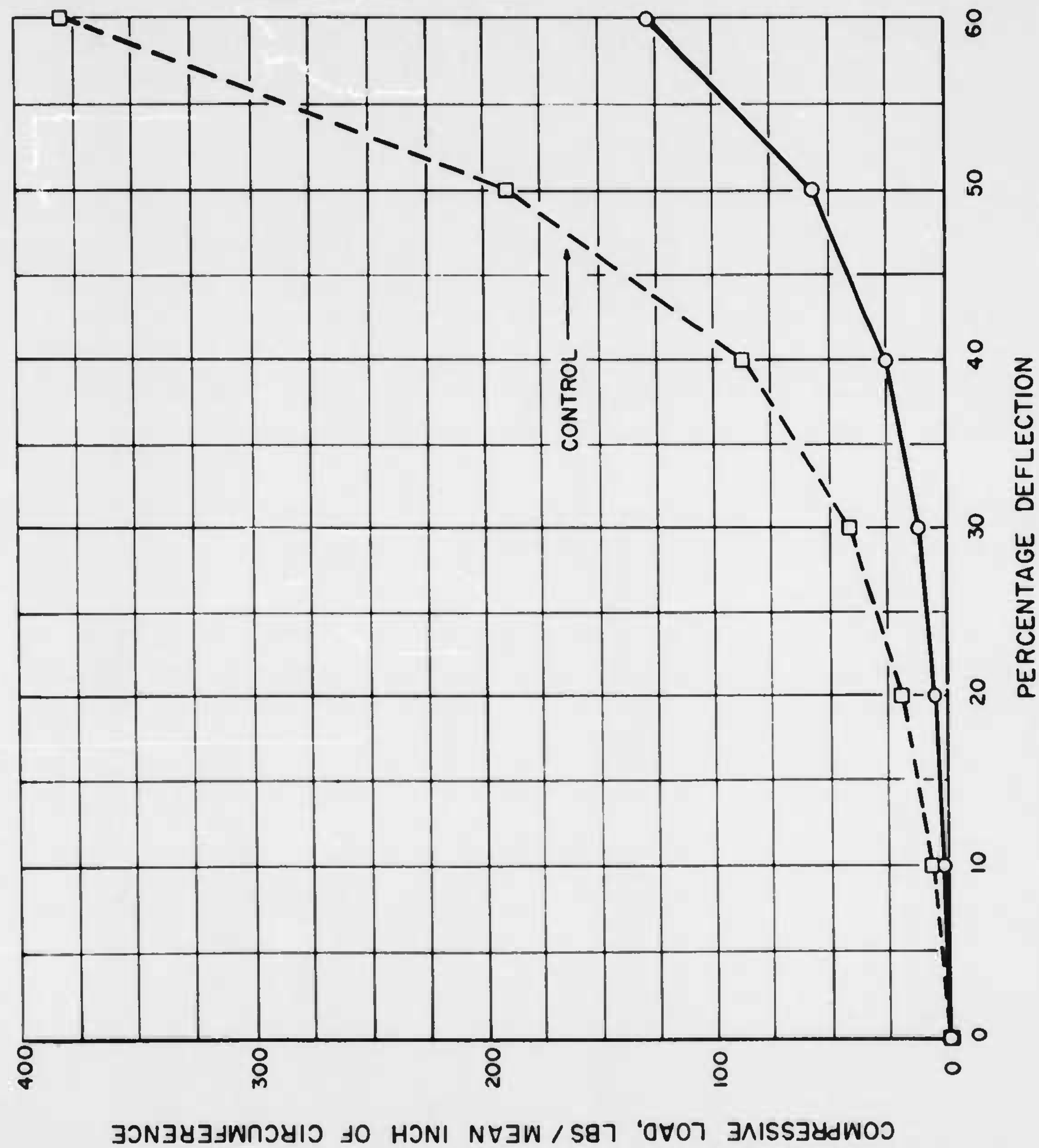


Figure 30. Compressive Load vs Percentage Deflection of AN 6227-21 O-Ring

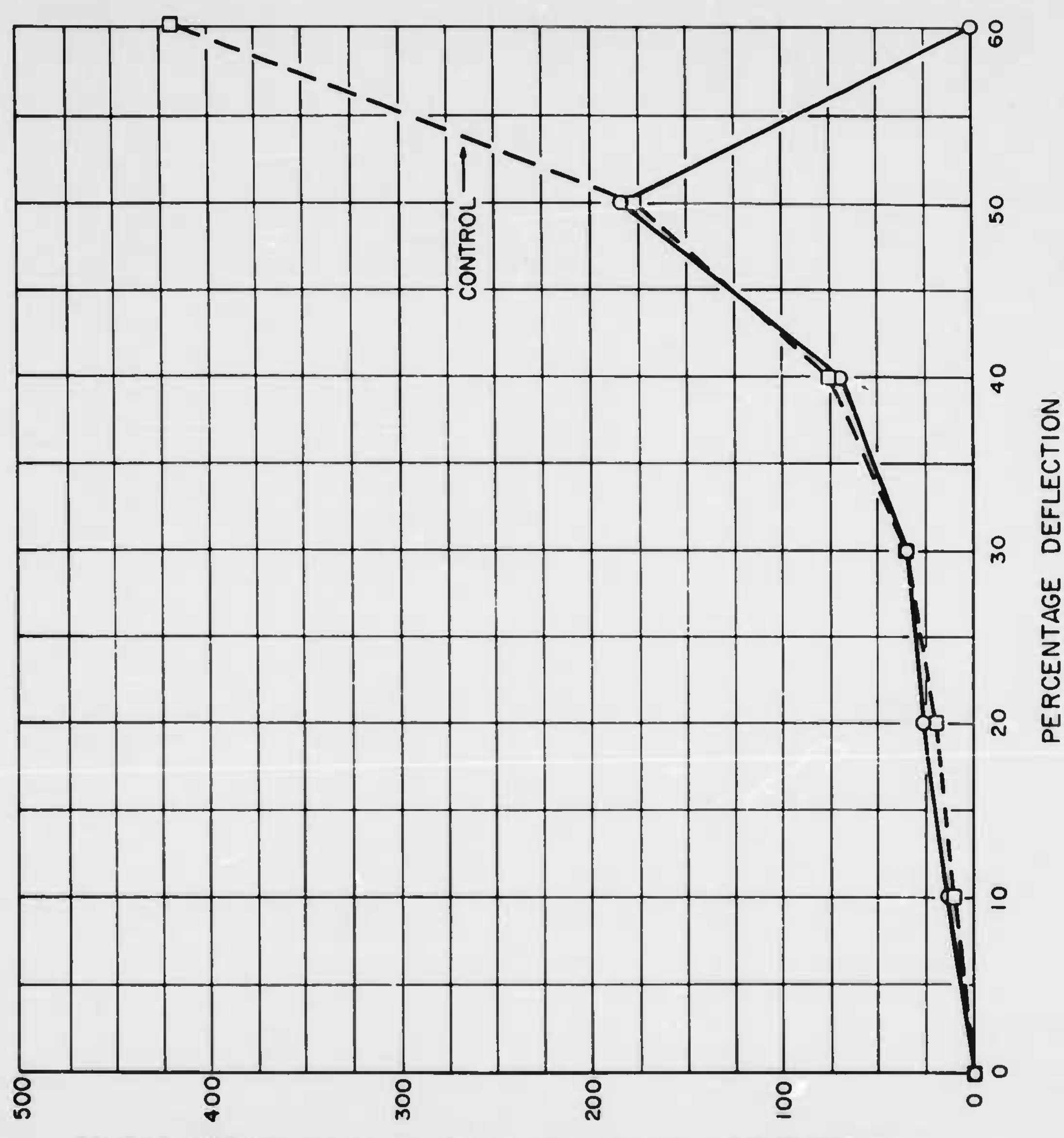


Figure 31. Compressive Load vs Percentage Deflection of MS28778-8 O-Ring

CONCLUSIONS AND RECOMMENDATIONS

RECOMMENDATIONS FOR FUTURE WORK

The work on the present program has uncovered several areas and topics concerning O-ring aging and associated problems that should be explored to gain further insight into O-ring aging characteristics. This section includes discussions of these areas and Rocketdyne's suggestions concerning the direction of future studies.

Study of O-rings in Cryogenic Systems

As a result of the findings of this study, it appears that O-ring (MS28778) properties change as a result of cryogenic exposure in a nonoxidizing environment. Further studies should be performed on a larger sampling of O-rings to definitely confirm these findings. In addition, studies should be conducted to provide explanations for such changes in properties to ultimately provide a solution to the problem of having a harder, less-resilient ring after exposure to cryogenic temperatures.

The direction of this latter study should emphasize the effect of the low temperatures on the plasticizer in the O-ring.

Development of Test Methods for Identifying O-Ring Manufacturer on Noncolor-Coded O-Rings

The results of this study indicate conclusively that there are definite differences in the aging rates of O-rings molded by different manufacturers. This finding provides impetus for not only maintaining color-code identification of suppliers, but also for requiring color coding of rings made to those specifications which do not currently require manufacturer designation codes. Because of the fact that some O-rings do not have color-code markings, it has been suggested that test methods be developed to ascertain the manufacturer on such rings. A possible method for achieving this would be one utilizing a Beckman IR4 infrared spectrophotometer to detect different infrared peaks, if any exist, in the compounds from the different manufacturers.

Modification of Test Methods

The standard ASTM Compressive Stress and Compression-Set test methods utilize button-type samples rather than O-rings. It was found in this study, using O-rings, that the precision of measurements of these properties is somewhat poor. Therefore, methods and procedures should be developed to permit accurate and precise measurement of these properties, which are related to the O-ring sealing mechanism, on O-ring samples.

Evaluation of the Sensitivity of Various Properties to Aging

Emphasis has been placed in all of the studies conducted in this program on the use of physical property tests in providing indications of aging. It would be beneficial to also consider developing and utilizing special techniques and tests which may be better aging indicators (and more sensitive to aging) than physical property tests. Such techniques and tests might include oxygen absorption, infrared and X-ray analysis, and solvent extraction methods. Following is a brief discussion on some of these techniques and suggestions concerning the performance of such tests.

Oxygen Absorption. It is generally recognized that the principal cause of deterioration of elastomers is oxidation. Investigators have attempted to correlate the rate of oxygen intake (absorption) by an elastomer stock with the extent of deterioration caused by aging. From the results of several studies (Ref. 31 and 32), it appears that oxygen absorption rates may be correlated to some extent with degradation of physical properties and may qualify as a criterion of aging resistance.

Basically, oxygen absorption apparatus may be classified as the gravimetric (in which the increase in weight of the sample due to oxygen absorption is measured), the manometric (in which the drop in oxygen pressure in a closed system is recorded), and the volumetric (in which the change in volume at constant pressure is recorded). The gas is generally pure oxygen and the temperatures are fairly high (generally 250 F).

Shelton (Ref. 33) and other investigators appear to favor the volumetric method because of fewer complications and better reproducibility. A small ground rubber sample (approximately 1.5 grams) is placed in an oil bath, maintained at 250 F (or other predetermined temperature). Pure oxygen is introduced into the system and as the oxygen is absorbed by the rubber, a leveling bulb is adjusted until the mercury levels are even (indicating atmospheric pressure). The volume of oxygen absorbed after a definite time period may, therefore, be measured and the results are expressed as millimeters of oxygen per gram sample per hour. A plot of oxygen absorption vs time is generally useful to indicate the autocatalytic nature of the oxidation of the material, i.e., the rate becomes faster as the extent of oxidation increases. Juve (Ref. 34) has plotted data in terms of rate of absorption vs extent of oxidation. With this type of plot, two parameters can be used to characterize the oxidation behavior of the material, one being the rate at zero time, and the other the slope of the resulting straight line which is a measure of the autocatalytic tendency.

The major objection to the oxygen absorption test has been that at the high temperature required to perform the absorption test rapidly, the oxidation mechanism may be different from that at service temperatures. However, in comparing similar vulcanizates, the mechanisms of degradation would also be similar, and thus valid comparisons could still be made.

Preliminary investigations to determine if the routine, rapid volumetric measurement of rates of oxygen absorption of O-ring samples adequately correlate with the degradation of their mechanical properties is suggested. O-ring samples artifically aged to obtain various degrees of degradation would be ground in a mill after their physical properties were determined. Triplicate absorption measurements would be made.

Chemical Tests. The aging of elastomers is accompanied by distinct chemical changes: further crosslinking and polymerization, chain scission, and/or alteration of the chemical nature of the side groups. These chemical changes are not only reflected in degraded physical properties, which are the basic means currently used for determining aging, but also in the inherent molecular structure of the elastomer. It would, therefore, appear to be quite possible to employ chemical tests, utilizing instrumental analysis, in some cases, to detect these changes due to aging. All of the suggested tests described in the following paragraphs would be of an exploratory nature and would be run to determine the feasibility of utilizing such tests as rapid, accurate methods to be correlated with degraded physical properties.

Infrared Absorption Study. Actual infrared absorption spectrums from compressed samples of aged and unaged O-rings would be studied, and the difference in peaks would be observed to determine the extent of breakdown of various ingredients in the vulcanizates (especially antioxidants). The usual method is to take the structures proposed and note the bands which would be expected for each on a basis of the general knowledge available. The analyses can be performed using a Beckman IR4 infrared spectrophotometer.

X-Ray Pattern Analysis Study. X-ray pattern analysis is another fundamental study which would be run to determine if the amorphous or crysalline regions in a sample are either destroyed or increased to any extent because of aging.

Solvent Extraction Studies. The solubility of the elastomer will also be affected by changes in the molecular structure.

Solvent extractables of compounded rubber O-rings should increase as aging proceeds due to chain scission and gradual lowering of the overall molecular weight. Comparison of extractables between O-rings of identical compositions before and after aging could be of beneficial values.

Good rubber solvents of the aromatic variety, e.g., toluene or benzene, will be the starting point for this investigation although other solvents may prove more useful. Solvent refluxing through a ground rubber sample in a porous thimble (Soxhlet extractor) will give extractables that might be a measure of molecular breakdown. The percent of rubber retained in each thimble will be accurately measured after drying to a constant weight. The solvent refluxing itself would continue for 10 to 24 hours until a constant value is obtained. In addition, the extracted portion would be examined by infrared spectrophotometry for additional information on the scission products.

The methods described are commonly used laboratory procedures for polymer studies, but have not been ordinarily used in conjunction with aging studies.

Evaluation of Superior Age-Resistant O-Ring Compounds

Polymers with superior aging characteristics to Buna-N are available. These include, among others, the fluoropolymers (Viton and Fluorel), silicone rubber, and the ethylene-propylene copolymers. However, compounds utilizing these base elastomers are generally deficient in certain physical properties which are quite necessary in liquid-rocket-engine applications.

The evaluation of new elastomeric formulations, including Viton compounds submitted by rubber molders, to basic property tests of the military specifications, as well as to aging tests is suggested. Various molders have indicated that they anticipate and forsee and, in some cases, have developed compounds utilizing age-resistant elastomers that will meet many of the requirements of the military O-ring specifications.

A second approach will be to evaluate new basic elastomers which have been developed very recently. A considerable amount of effort has been and is being expended in developing stereospecific elastomer systems. These elastomers are produced by a controlled polymerization through special catalyst techniques and are distinguished from other rubber materials by their highly oriented and highly spatial configuration. Generally, the oriented elastomers are noted for improved physical properties over their "unoriented" counterparts, and for the uniformity of the vulcanization process. This latter feature results in a more homogeneous material and also in improved low-temperature characteristics. It is also anticipated that because of the more uniform and homogeneous material, the aging process would progress uniformly throughout the elastomer. Whereas, in unoriented elastomers, aging generally produces varying concentrations of crosslinked regions throughout the materials and subsequent "weak spots", as far as highly crosslinked and brittle, unextensible areas are concerned, stereospecific elastomers do not exhibit such behavior. Therefore, the aging process would not affect the material as greatly, or as soon, in oriented polymers as they would in random-polymerized compounds.

Stereospecific polymers are commercially available (polybutadiene and polyisoprene). Laboratory batches of stereospecific copolymers of polybutadiene and acrylonitrile are also available.

A program to evaluate these new basic elastomers is suggested. The synthesis and compounding efforts to the requirements provided would be performed best by the rubber companies currently conducting research on oriented polymers.

Evaluation of Aging Requirements of O-Ring Military Specification

Although the military specifications for O-rings cover such things as physical property evaluations and packaging requirements, they fail to provide aging parameters for establishing an O-ring service life. A military age-control specification does exist (ANA Bulletin No. 438A), but this document controls the age limits of synthetic rubber parts up to the delivery of the aircraft or missile system to the government. Efforts have been made by various governmental agencies to rectify this situation by incorporating a service life limit in one specification to cover all synthetic elastomers. These efforts have been unsuccessful because they failed to actually establish aging parameters in determining the service life limits of particular elastomeric compounds. For example, the same aging limitations should not be imposed upon known, highly age-resistant materials such as silicones, fluorosilicones, and fluorinated elastomers, as upon relatively less age-resistant materials such as natural rubber, butadiene-styrene, and butadiene-acrylonitrile.

Investigations and exploration into the use of various tests for inclusion in specifications which will ensure procurement of elastomeric O-rings having a maximum service life compatible with the other necessary characteristics needed in O-rings are suggested. From the results of some of the studies conducted in other phases of the over-all O-ring aging program, recommendations would be in order as to the feasibility of including any one aging-property test or series of tests into elastomer specifications.

A second possibility is to suggest and present a special O-ring specification for ballistic missile applications or a "Recommended Practice" O-ring age-control document (similar to ASTM "Recommended Practices") covering the particular needs and requirements of SAC and SBAMA.

REFERENCES

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    c. MIL-P-5516B Packing and Gaskets, Preformed, Petroleum-Hydraulic Fluid Resistant

    d. MIL-P-25732A Packing, Preformed, Petroleum-Hydraulic Fluid Resistant, 275 F.

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APPENDIX A

COMPLETE TENSILE AND ELONGATION DATA FOR
CRYOGENIC EXPOSURE STUDY (10 CYCLES AND 20 CYCLES)

O-Ring Type	Condition Imposed	Ultimate Tensile Strength, psi	Elongations, %	Hardness Shore-A
MS28778-16	Control	1570	110	80
		1245	122	80
		1330	100	81
		1650	100	80
		1640	118	79
		1405	104	80
		1520	116	80
		1440	105	80
		1550	110	80
MS28778-16	Unstressed, 10 Cryogenic Cycles	1815	110	80
		1091	100	80
		1530	105	80
		1641	110	80
		1470	108	80
MS28778-16	15% Stretch, 10 Cryogenic Cycles	1785	109	82
		1500	109	82
		1632	100	83
		1500	100	82
		1580	107	81
MS28778-8	Control	1655	106	80
		1875	105	80
		1700	100	80
		1655	103	--
		1410	104	--

	Cryogenic Cycles	1091	100	80
		1530	105	80
		1641	110	80
		1470	108	80
MS28778-16	15% Stretch, 10 Cryogenic Cycles	1785	109	82
		1500	109	82
		1632	100	83
		1500	100	82
		1580	107	81
MS28778-8	Control	1655	106	80
		1875	105	80
		1700	100	80
		1655	103	—
		1410	104	—
MS28778-8	Unstressed, 10 Cryogenic Cycles	1310	104	80
		1550	105	80
		1300	100	80
		1820	110	—
		1554	105	—
MS28778-8	15% Stretch, 10 Cryogenic Cycles	1820	106	82
		1700	100	82
		1490	90	83
		1825	100	81
		1415	90	82
MS28778-16	Unstressed, 20 Cryogenic Cycles	1988	101	80
		1716	101	81
		1520	84	80
		1617	86	81
		1780	105	80
MS28778-16	15% Stretch, 20 Cryogenic Cycles	2120	98	83
		1802	95	82
		1972	99	82
		1901	103	83
		1530	87	82
		1675	99	83
		1720	89	82

FORM R 18-G-18

R-5253

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APPENDIX B

COMPLETE COMPRESSIVE LOAD AND COMPRESSION SET DATA
FOR CRYOGENIC EXPOSURE STUDY (10 CYCLES)

Condition	Loads for O-Rings, pounds (for the following deflections,%) 10	20	30	40	50	60		Deflection, %	Compression Set, %
MS28778-16									
Control	91	176	317	582	1080	2230		35.0	43.7
	78	178	323	590	1140	2500		35.0	41.3
	73	156	286	520	1020	2250		35.0	37.5
	75	160	294	530	992	2000		35.0	40.0
								35.0	42.5
Average	79	168	305	556	1057	2240			
							Average	35.0	41.0
Unstressed,10 Cryogenic Cycles	62	142	261	480	872	1645			
	76	161	298	535	1010	2150			
	80	163	298	530	1028	2225		34.5	33.4
	71	156	290	539	1060	2390		34.5	33.4
Average	72	156	287	520	993	2100	Average	34.5	33.4
15% Stretch, 10 Cryogenic Cycles	43	112	222	419	746	1600		34.0	31.5
	54	133	250	454	850	1755		34.0	26.3
	54	131	245	454	847	1650		34.0	31.5
	46	120	230	435	820	1635		34.0	31.5
	52	128	242	438	775	1460		34.0	26.3
Average	50	125	238	440	809	1620	Average	34.0	29.4
MS28778-8									
Control	31	71	130	223	425	930		35.7	46.6
	36	80	146	265	525	1240		35.7	46.6
	[illegible]	76	134	240	450	980		35.7	[illegible]

	71	156	290	539	1060	2390		34.5	33.4
Average	72	156	287	520	993	2100	Average	34.5	33.4
15% Stretch, 10 Cryogenic Cycles	43	112	222	419	746	1600		34.0	31.5
	54	133	250	454	850	1755		34.0	26.3
	54	131	245	454	847	1650		34.0	31.5
	46	120	230	435	820	1635		34.0	31.5
	52	128	242	438	775	1460		34.0	26.3
Average	50	125	238	440	809	1620	Average	34.0	29.4
MS28778-8									
Control	31	71	130	223	425	930		35.7	46.6
	36	80	146	265	525	1240		35.7	46.6
	37	76	134	240	450	980		35.7	46.6
	38	77	138	245	475	1100		35.7	46.6
	35	76	138	250	520	1480		35.7	40.0
Average	35	76	137	245	480	1140		35.7	40.0
Unstressed, 10 Cryogenic Cycles	30	65	120	217	418	985		36.5	32.2
	29	65	120	212	403	905		36.5	32.2
	36	77	140	256	515	1190		36.5	32.2
	28	63	118	214	420	965		36.5	32.2
	29	66	124	228	437	1020		36.5	32.2
Average	30	67	124	225	438	1014	Average	36.5	32.2
15% Stretch, 10 Cryogenic Cycles	26	62	115	210	425	1020		34.2	25.0
	26	60	114	208	402	880		34.2	28.6
	27	67	132	250	495	1125		34.2	28.6
	25	57	108	197	400	930		34.2	28.6
	29	65	123	225	436	928		34.2	25.0
Average	26	62	118	218	430	978	Average	34.2	27.2

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APPENDIX C

COMPLETE COMPRESSION RELAXATION DA

MS28778-16 O-RINGS (20% COMPRESS

Condition	Initial Load, pounds	Immediate Load Drop, pounds
Control	158	143
	150	136
	153	140
	154	139
	142	131
Average	152	138
Unstressed, 20 Cryogenic Cycles (Tested Immediately After Exposure)	153	141
	151	139
	139	128
	141	130
	141	130
Average	145	134
Unstressed, 20 Cryogenic Cycles (Tested 5 Days After Exposure)	148	136
	158	146
	132	122
	143	133
	159	146
Average	148	137
15% Stretch, 20 Cryogenic Cycles	143	131
	143	132
	129	120
	133	121
	138	128
Average	137	126
Old Serviced MS28778-16 O-Ring From LOX Start Tank	86	74

APPENDIX C

LETE COMPRESSION RELAXATION DATA

8778-16 O-RINGS (20% COMPRESSION)

Load, s	Immediate Load Drop, pounds	Immediate Load Loss, %	Final Load After 15 Minutes	Total Drop After 15 Minutes, %
	143	9.5	110	30.3
	136	9.4	104	30.6
	140	8.6	107	30.0
	139	9.6	108	29.8
	131	7.7	99	30.4
	138	9.0	106	30.2
	141	7.7	111	27.5
	139	7.7	110	27.2
	128	7.7	101	27.4
	130	7.7	103	27.0
	130	7.7	103	27.0
	134	7.7	106	27.2
	136	8.0	106	28.5
	146	7.7	114	27.8
	122	7.7	96	27.4
	133	7.1	106	25.8
	146	8.0	115	27.7
	137	7.7	107	27.5
	131	8.4	103	27.9
	132	7.7	104	27.3
	120	7.1	94	27.2
	121	9.0	95	28.6
	128	7.3	101	26.8
	126	7.9	99	27.6
	74	14	64	24.4

APPENDIX D

COMPLETE TEST DATA ON SPECIALLY FORMULATED COMPOUNDS PLASTICIZED AND UNPLASTICIZED

O-Ring Type	Condition	50% Tensile Stress, psi	Elongation, %	Tensile Strength, psi
Plasticized	Control	290	165	2150
		300	180	2270
		360	165	1830
		325	175	2070
		365	160	1750
	Average	328	169	2010
	15% Stretch, 20 Cryogenic Cycles	438	---	----
		508	126	1640
		432	147	1830
	Average	438	136	1735
Unplasticized	Control	550	130	1890
		442	120	1830
		597	120	1815
		617	130	2010
		588	110	1620
	Average	558	122	1830
	15% Stretch, 20 Cryogenic Cycles	750	138	2700
		725	119	1825
		700	108	1735
	Average	725	121	2087

APPENDIX E

COMPLETE PHYSICAL PROPERTY DATA OF MS28778-16 O-RINGS
AFTER EXPOSURE TO OXYGEN ATMOSPHERE

Condition		Tensile Strength, psi	Compressive Loads for MS O-rings, pounds (for the following deflections,%)					
			10	20	30	40	50	60
Control		1571	76	161	292	523	987	2080
		1245						
		1330						
		1650						
		1640						
		1405						
		1520						
		1440						
		1550						
	Average	1483						
Unstressed Rings in O_2 Atmosphere[2]		1475	68	142	253	430	730	1340
		1555	73	154	270	465	843	1700
		1480	71	154	270	470	850	1760
		1348	72	156	278	485	870	1720
		1470	72	154	270	480	890	1900
	Average	1465	71	152	268	466	837	1680
15% Stretched Rings in O_2 Atmosphere[2]		1610	73	159	295	535	1030	1470
		1556	60	137	250	440	790	1475
		1378	55	130	245	440	805	1555
		1175	65	146	265	470	870	1480
		1530	63	142	255	465	870	1348
	Average	1450	63	143	262	470	874	1464

APPENDIX F

SOFT GOODS ANALYSIS TEST FORMS AND DATA SHEETS

ANALYSIS TEST FORMS

All O-ring test data are entered on the Soft Goods Analysis Test Form (Fig. F-1).

To avoid confusion in keypunching, the following steps will be taken to ensure clarity and to distinguish letters from integers:

1. Print all words in capital letters.
   (Thus, Engine No. is printed as ENGINE NO.)
2. Certain letters and integers that could be confused are written as follows:

Letter	Modified by Adding	To Avoid Confusion with the Similar Integer
O	Slash (Ø)	0
I	Horizontal Bars (I)	1
Z	Horizontal Bar (Ƶ)	2
S	Vertical Bar ($)	5
C	Vertical Bar (¢)	--

3. All series of integers will be placed in the appropriate block as far to the right as possible except for part number, identification, Illustrated Parts Breakdown (IPB) location, engine number, IPB number, part description, and area; in these areas, integers will be placed to the left. Thus, if the engine number is shorter

SOFT GOODS ANALYSIS TEST FORM

① PART NUMBER	⑦ IDENT 12	13 IPB LOCATION 18	19 ENGINE NO. 24	25 IPB NUMBER 31	32 PART DESCRIPTION 38	CM	41 CM	CM 48			
	47 CM	CM 54	CM 58	CONT TM	62 ACT TM	CONT ELONG	ACT ELONG	CONT T LD 74	75 TEN LD 78	CARD ID	0 1
① SAME AS ABOVE	13 IPB LOCATION 18	19 ENGINE NO. 24	MIN SPEC WD	MAX SPEC WD	CONT WD	34 ACT WD	NOM WD 39	MIN SPEC HD	MAX SPEC HD	CONT HD	ACT
	HD	48 NOM ID	AREA 55	TS SPEC 59	60 CONT AREA	REMARKS 72	RECORD ID				0 2
① PART NUMBER	⑦ IDENT 12	13 IPB LOCATION 18	19 ENGINE NO. 24	25 IPB NUMBER 31	32 PART DESCRIPTION 38	CM	41 CM	CM 46			
	47 CM	CM 54	CM 58	CONT TM	62 ACT TM	CONT ELONG	ACT ELONG	CONT T LD 74	75 TEN LD 78	CARD ID	0 1
① SAME AS ABOVE	13 IPB LOCATION 18	19 ENGINE NO. 24	MIN SPEC WD	MAX SPEC WD	CONT WD	34 ACT WD	NOM WD 39	MIN SPEC HD	MAX SPEC HD	CONT HD	ACT
	HD	48 NOM ID	AREA 55	TS SPEC 59	60 CONT AREA	REMARKS 72	RECORD ID				0 2
① PART NUMBER	⑦ IDENT 12	13 IPB LOCATION 18	19 ENGINE NO. 24	25 IPB NUMBER 31	32 PART DESCRIPTION 38	CM	41 CM	CM 46			
	47 CM	CM 54	CM 58	CONT TM	62 ACT TM	CONT ELONG	ACT ELONG	CONT T LD 74	75 TEN LD 78	CARD ID	0 1
① SAME AS ABOVE	13 IPB LOCATION 18	19 ENGINE NO. 24	MIN SPEC WD	MAX SPEC WD	CONT WD	34 ACT WD	NOM WD 39	MIN SPEC HD	MAX SPEC HD	CONT HD	ACT
	HD	48 NOM ID	AREA 55	TS SPEC 59	60 CONT AREA	REMARKS 72	RECORD I.O.				0 2
① PART NUMBER	⑦ IDENT 12	13 IPB LOCATION 18	19 ENGINE NO. 24	25 IPB NUMBER 31	32 PART DESCRIPTION 38	CM	41 CM	CM 48			
	47 CM	CM 54	CM 58	CONT TM	62 ACT TM	CONT ELONG	ACT ELONG	CONT T LD 74	75 TEN LD 78	CARD ID	0 1
① SAME AS ABOVE	13 IPB LOCATION 18	19 ENGINE NO. 24	MIN SPEC WD	MAX SPEC WD	CONT WD	34 ACT WD	NOM WD 39	MIN SPEC HD	MAX SPEC HD	CONT HD	ACT
	HD	48 NOM ID	AREA 55	TS SPEC 59	60 CONT AREA	REMARKS 72	RECORD ID				0 2
① PART NUMBER	⑦ IDENT 12	13 IPB LOCATION 18	19 ENGINE NO. 24	25 IPB NUMBER 31	32 PART DESCRIPTION 38	CM	41 CM	CM 48			
	47 CM	CM 54	CM 58	CONT TM	62 ACT TM	CONT ELONG	ACT ELONG	CONT T LD 74	75 TEN LD 78	CARD ID	0 1
① SAME AS ABOVE	13 IPB LOCATION 18	19 ENGINE NO. 24	MIN SPEC WD	MAX SPEC WD	CONT WD	34 ACT WD	NOM WD 39	MIN SPEC HD	MAX SPEC HD	CONT HD	ACT
	HD	48 NOM ID	AREA 55	TS SPEC 59	60 CONT AREA	REMARKS 72	RECORD ID				0 2
① PART NUMBER	⑦ IDENT 12	13 IPB LOCATION 18	19 ENGINE NO. 24	25 IPB NUMBER 31	32 PART DESCRIPTION 38	CM	41 CM	CM 48			
	47 CM	CM 54	CM 58	CONT TM	62 ACT TM	CONT ELONG	ACT ELONG	CONT T LD 74	75 TEN LD 78	CARD ID	0 1
① SAME AS ABOVE	13 IPB LOCATION 18	19 ENGINE NO. 24	MIN SPEC WD	MAX SPEC WD	CONT WD	34 ACT WD	NOM WD 39	MIN SPEC HD	MAX SPEC HD	CONT HD	ACT
	HD	48 NOM ID	AREA 55	TS SPEC 59	60 CONT AREA	REMARKS 72	RECORD ID				0 2
① PART NUMBER	⑦ IDENT 12	13 IPB LOCATION 18	19 ENGINE NO. 24	25 IPB NUMBER 31	32 PART DESCRIPTION 38	CM	41 CM	CM 48			
	47 CM	CM 54	CM 58	CONT TM	62 ACT TM	CONT ELONG	ACT ELONG	CONT T LD 74	75 TEN LD 78	CARD ID	0 1
① SAME AS ABOVE	13 IPB LOCATION 18	19 ENGINE NO. 24	MIN SPEC WD	MAX SPEC WD	CONT WD	34 ACT WD	NOM WD 39	MIN SPEC HD	MAX SPEC HD	CONT HD	ACT
	HD	48 NOM ID	AREA 55	TS SPEC 59	60 CONT AREA	REMARKS 72	RECORD ID				0 2

TEST FORM FROM 11-1-62 THROUGH 1-1-63

Figure F-1. Soft Goods Analysis Test Form than six spaces (such as J4501), it will be entered to the left, leaving blank the last space to the right. Any numerical entry (such as control elongation) which does not fill the spaces allotted for it (i.e., an elongation of 90%) will be entered so that the empty space is to the left of the first digit.

4. Some values require decimal points, i.e., tensile modulus (TM), tensile strength (TS), cross section or W-diameter (WD), nominal inside diameter, and area. Since the relative position of the decimal point does not change for TM or TS, the point is indicated by a dotted line in the case of TM and by actual point in the case of TS. The decimal point for nominal inside diameter will change the position so that it should be entered in the space in which it falls. Thus, an inside diameter of 1.05 is entered as |1|.|0|5|, with the decimal point taking up a space. If the decimal point comes before the number, it is to be entered, and the number written according to rule 3 above, i.e., |0|.|9|4|.
5. All entries must be written with pencil (No. 2 hardness or harder).
6. All components that are not O-rings (backups, gaskets, etc.) are to be entered on separate sheets specially prepared for non O-ring components (Fig. F-2).

DATA SHEETS

All spaces or multiples of spaces are identified by column number at start or finish.

SOFT GOODS ANALYSIS TEST FORM
NON O-RING COMPONENTS

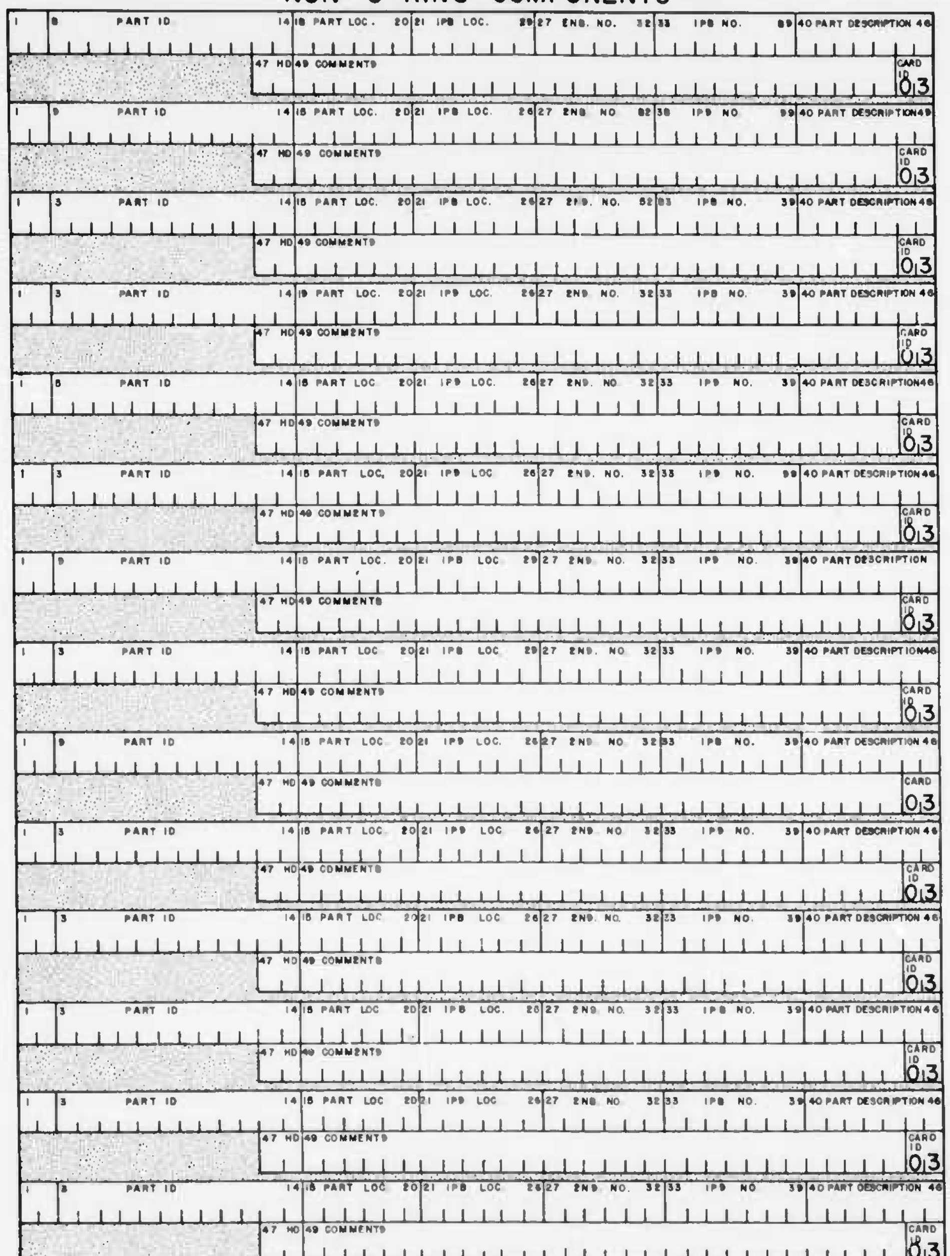


Figure F-2. Soft Goods Analysis Test Form
(Non O-Ring Components)

Part Number, Identification Columns 1 through 12)

Columnsl through 12, part number and identification, will be filled with the following information:

1. Columns 1 through 6 are used for the last two numbers of the O-ring series identification, with a dash followed by the three identifying size numbers of the particular O-ring. Thus:

    a. MS28778-200 will be written as 78-200. Any O-ring with less than three digits after the dash shall be written as |7|8|-|2| | | with blank spaces following the digit after the dash.

    b. Columns 7 through 12 are used for the abbreviated component location of the ring. The following component locations only shall be used and may be abbreviated as shown:

Location	Abbreviation
1. Major Components System	MCS
2. Pneumatic Control System	PCS
3. Lubrication System	LS
4. Gas Generator System	GGS
5. Start System	SS
6. Hydraulic System	HS
7. Propellant Feed System	PFS
8. Exhaust System	ES

IPB Location (Columns 13 through 18)

Columns 13 through 18 are used for the figure number (columns 13 and 14), a dash (column 15), and the location on the figure (columns 16, 17, and 18) of the part in the applicable IPB. Thus, the entry 33-123 represents Figure 33, part number 123, on that figure in the IPB.

Engine No. (Columns 19 through 24)

Columns 19 through 24, are to be used for the number of the engine being examined. The different types of engines appear as follows:

Engine No.	Type of Engine
J4080	Jupiter
004090	Thor
112090	Booster, Atlas
222090	Sustainer, Atlas
330481	Vernier, Atlas, or Thor

IPB Number (Columns 25 through 31)

Columns 25 through 31 will be used for the latest revision date of the applicable IPB. Thus, if the IPB was revised on 10 June 1962, it would be written as 620610, representing the year, month, and day of the revision.

Part Description (Columns 32 through 38)

Columns 32 through 38 will be used for the verbal description of the tested part. The descriptive word is limited to seven letters. The following are examples of words used: packing (for 0-ring), seals, gaskets, backups. Parts other than 0-rings shall be entered on a separate test form with separate instructions.

CM (Columns 38 through 58)

Columns 38 and 39, 41 through 43, 44 through 46, 47 through 50, 51 through 58 will be used for compressive modulus data. The load (in pounds) at 10% deflection is placed in columns 38 and 39, the load (in pounds) at 20% deflection is placed in columns 41 through 43, etc. Each group of columns represents a load value from 10% by multiples of 10 to 60%. If the entry is smaller than the number of spaces allotted for it, the entry will be placed as far as possible to the right, with the blank spaces coming before the entry.

Cont. TM, Act. TM (Columns 59 through 64)

Columns 59 through 61 and 62 through 64 will be used for control and actual load (in pounds) at 100% extension. The actual load values, to one decimal place, will be written with the figure following the decimal appearing after the dotted (or broken) vertical line. The dotted line serves as the decimal point.

Cont. Elong., Act. Elong. (Columns 65 through 70)

Columns 65 through 67 and 68 through 70 will be used for the control elongation at failure and the actual elongation at failure; these entries are in percent.

Cont. T. ID., Ten. ID. (Columns 71 through 78)

Columns 71 through 74 and 75 through 78 will be used for the control values and the actual values of tensile load at failure, expressed in pounds for a single strand. (If the ring is placed over drums and tested as a ring, the value obtained must be divided by 2.)

Card ID (Columns 78 through 80) is to be left blank.

There are four lines used to describe an O-ring. The third line is filled out identically to the first line to column 24.

Min. Spec. WD, Nom WD (Columns 25 through 39)

Columns 25 through 39 will be used for the following: minimum specification W-diameter, maximum specification W-diameter, controls W-diameter, actual W-diameter, and nominal specification W-diameter. The decimal point is assumed to be at the left, and will not be entered.

Min. Spec. HD, Act. HD (Columns 40 through 47)

Columns 40 through 47 will be used for minimum specification hardness, maximum specification hardness, control hardness, and actual hardness in Shore-A Durometer units.

Nom. ID (Columns 48 through 51)

Columns 48 through 51 will be used for the nominal inside diameter from AN or MS drawing). The number will be placed in the spaces according to step 3 (page F-1) and the decimal point will occupy one space.

Area (Columns 52 through 55)

Columns 52 through 55 will be used for the cross-sectional area of the O-ring as determined from the nominal W-diameter. This number will always have a decimal point at the extreme left; therefore, this decimal point will not be entered, but will be assumed. This number will be placed always as far as possible to the left, and blank spaces, if any, will appear only after the number. The cross-sectional area will be entered with only three significant digits. Thus, an area of 0.034967 (the cross-sectional area of a ring having a W-diameter of 0.212) will be entered as |0|3|5|0|.

TS Spec. (Columns 56 through 59)

Columns 56 through 59 are to be left blank.

Cont. Area (Columns 60 through 63)

Columns 60 through 63 will be used for the area of the control O-rings. This area will be determined from the attached table which lists control specification and nominal values.

Remarks (Columns 64 through 70)

Column 64 through 70 will be used for remarks describing any unusual condition of the O-ring or part (e.g., dirty, cracked, broken, chipped, etc.).

Record ID (Columns 73 through 78)

Column 73 through 78 shall be left blank.

NON O-RING COMPONENTS ANALYSIS TEST FORMS

Columns 1 and 2

Columns 1 and 2 will be used for any one- or two-digit number from 01 to 99. This number distinguishes non O-ring components from each other and from the O-rings.

Part ID (Columns 3 through 14)

Columns 3 through 14 will be used for the identification number of the part. If the part number is longer than the spaces alloted for it, an abbreviation will be determined for each individual case.

Part Loc. (Columns 15 through 20)

Columns 15 through 20 are to be used for the abbreviated location of the ring. The same abbreviations and format shall be used as is described in rule 1b (page F-5).

IPB Loc. (Columns 21 through 26)

Columns 21 through 26 will be used for the figure and part number appearing in the applicable IPB. This entry shall be as described under IPB Location, page F-6.

Eng. No. (Columns 27 through 32)

Columns 27 through 32 will be used for the engine number of the engine being examined and shall be entered as described under Engine No., page F-6.

IPB No. (Columns 33 through 39)

Columns 33 through 39 will be used for the applicable IPB number and shall be entered as described under IPB Number, page F-6.

Part Description (Columns 40 through 48)

Columns 40 through 48 will be used for the verbal description of the tested part according to the information given under Part Description, page F-7. The following entries to be used are: backup, gasket, washer, seal, ring lipseal, etc.

HD (Columns 47 and 48)

Columns 47 and 48 will be used for the hardness of the part in either Shore-D or Rockwell units as applicable.

Comments (Columns 49 through 78)

Columns 49 through 78 will be used for comments on the condition of the part; whether greasy, chipped, broken etc., and, if necessary, further descriptive materials about the part, i.e., if the part came from an uncoded location.

APPENDIX G

A STUDY OF THE STANDARD TENSILE TEST PERFORMED AT VARIOUS LOADING AND STRAIN RATES ON SEVERAL O-RING SIZES

Rocketdyne's Materials and Process Group conducted a study to determine whether tensile data obtained from O-rings with such variables as inside diameters, thickness, loading rate, and strain rate would produce variations greater than the permissible military specification limits of ±15%. Accumulation of data for all sizes of O-rings also will provide a background for determination of qualification values and tolerances.

The SAE G-4 (elastic seals) committee, of which Rocketdyne and the government agencies who are responsible for the specifications are members, recently discussed the possibility of changing the O-ring qualification test procedures in the military specifications. Almost all members of the committee were in general agreement that the specifications could be changed so that the purchasers of O-rings may perform their own receiving inspection, using O-ring tensile data as a criteria. However, there has not been enough work in this type of testing to establish actual tensile data for all sizes of O-rings. The current study is an effort to promote this needed background information in conjunction with testing being performed by other companies. It should be realized that much work and time will be required to accomplish these changes in the military specifications.

PROCEDURE

The first tensile study covered the testing of 20 different sizes of MS29513 O-rings with various diameters and thicknesses. This study was intended to determine the sensitivity of tensile data with variations of inside diameter and thickness, using one crosshead speed (20 inch/minute). These data are listed in Table G-1 and illustrated in Fig. G-1 through G-4 .

The second tensile study covered the testing of MS29513-218 size O-rings with five different crosshead speeds. This study varied the strain rate with inside diameter and thickness constant. These data are listed in Table G-2 and illustrated in Fig. G-5 through G-7.

In the third tensile study the MS29513-325 O-rings were tested with five different crosshead speeds. This study was made to compare the military specification test size O-ring (-325) to other sizes of O-rings to determine whether tensile data from any size O-ring is as consistant as that of the -325 size. These data are listed in Table G-3 and illustrated in Fig. G-8 through G-10.

Additional effort will be made in the near future in determining tensile data for AN-6290 O-rings.

DISCUSSION

Graphs of the O-ring data show that both the MS29513-218 and -325 O-rings are below the minimum elongation of 319% required by the QPL-5315-15 specification. Total elongation inadvertently was not recorded during tensile tests of the other sizes of O-rings.

Graphs of the tensile stress data show that the -325 size O-ring produces tensile strengths within the QPL5315-15 tensile stress limitations. However, all other sizes of O-rings that were tested produced

TABLE G-1

MS29513 O-RING DATA

(Varying Sizes)

O-Ring Size	ID, inch	W Diameter, inch	Ultimate Tensile Stress, psi	Time to 100% Elongation, minute	Strain Rate, in./in.-min	Tensile Stress at 100% Elongation, psi	Stress Rate, psi/min
– 15	0.551	0.070	1985	0.0486	20.6	625	12,850
– 15	0.551	0.070	1635			557	11,430
– 18	0.739	0.070	1595	0.0635	15.75	433	6,820
– 18	0.739	0.070	1615			466	7,350
– 19	0.801	0.070	1760	0.0685	14.6	329	4,880
– 19	0.801	0.070	1840			434	6,330
– 23	1.051	0.070	1735	0.088	11.4	430	4,890
– 23	1.051	0.070	1780			382	4,350
– 27	1.301	0.070	1595	0.107	9.35	268	2,500
– 27	1.301	0.070	1610			389	3,630
–112	0.487	0.103	1845	0.0462	21.6	658	14,250
–112	0.487	0.103	1882			592	12,800
–113	0.549	0.103	1770	0.0512	19.5	462	9,030
–113	0.549	0.103	1688			662	12,920
–115	0.674	0.103	1525	0.0610	16.4	450	7,380
–115	0.674	0.103	1530			607	9,950
–116	0.737	0.103	1675	0.066	15.15	450	6,820
–116	0.737	0.103	1685			372	5,640
–124	1.237	0.103	1905	0.105	9.52	403	3,840
–124	1.237	0.103	1895			449	4,280
–210	0.734	0.139	1640	0.0685	14.6	386	5,640
–210	0.734	0.139	1585			650	9,500
–219	1.296	0.139	1489	0.1122	8.91	514	4,580
–219	1.296	0.139	1380			425	3,785
–219	1.296	0.139	1556			365	3,280

-113	0.549	0.103	1688			662	12,920
-115	0.674	0.103	1525	0.0610	16.4	450	7,380
-115	0.674	0.103	1530			607	9,950
-116	0.737	0.103	1675	0.066	15.15	450	6,820
-116	0.737	0.103	1685			372	5,640
-124	1.237	0.103	1905	0.105	9.52	403	3,840
-124	1.237	0.103	1895			449	4,280
-210	0.734	0.139	1640	0.0685	14.6	386	5,640
-210	0.734	0.139	1585			650	9,500
-219	1.296	0.139	1489	0.1122	8.91	514	4,580
-219	1.296	0.139	1380			425	3,785
-219	1.296	0.139	1556			365	3,280
-235	3.109	0.139	1670	0.255	3.92	453	1,780
-235	3.109	0.139	1679			443	1,738
-239	3.609	0.139	1450	0.294	3.4	447	1,520
-239	3.609	0.139	1542			322	1,095
-239	3.609	0.139	1530			367	1,250
-242	3.984	0.139	1530	0.324	3.09	348	1,073
-242	3.984	0.139	1582			375	1,158
-247	4.609	0.139	970	0.374	2.68	459	1,260
-247	4.609	0.139	1027			331	885
-247	4.609	0.139	1088			320	856
-251	5.109	0.139	1485	0.413	2.42	738	1,785
-251	5.109	0.139	1899			685	1,660
-260	6.484	0.139	1820	0.513	1.95	643	1,252
-260	6.484	0.139	1810			640	1,249
-265	7.734	0.139	787	0.620	1.615	294	474
-265	7.734	0.139	834			265	428
-329	1.975	0.210	1638	0.1708	5.85	330	1,935
-329	1.975	0.210	1375			354	2,075
-329	1.975	0.210	1628			447	2,620

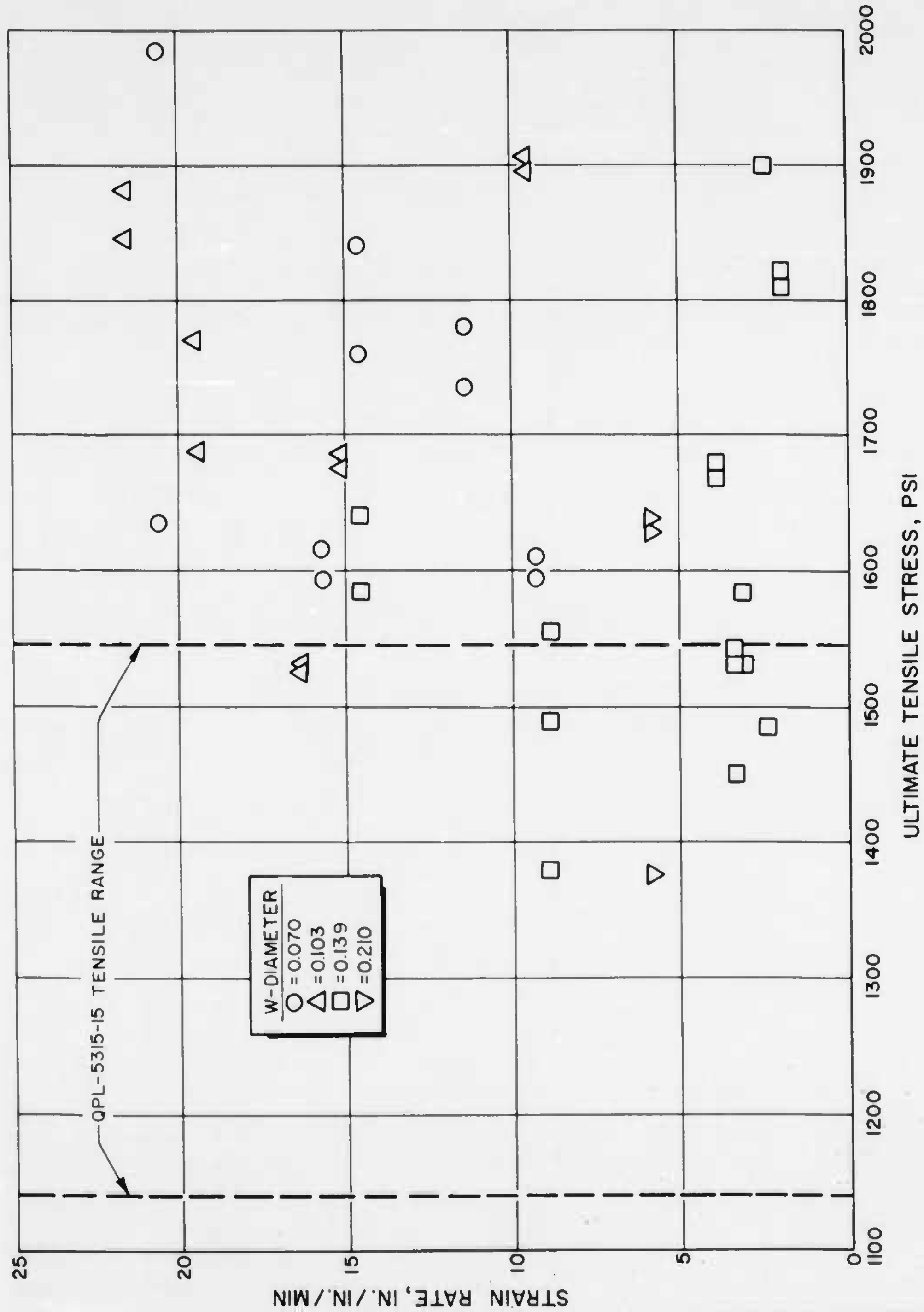


Figure G-1 Strain Rate vs Ultimate Tensile Strength of MS29513 O-Rings With Various Inside and W-Diameters

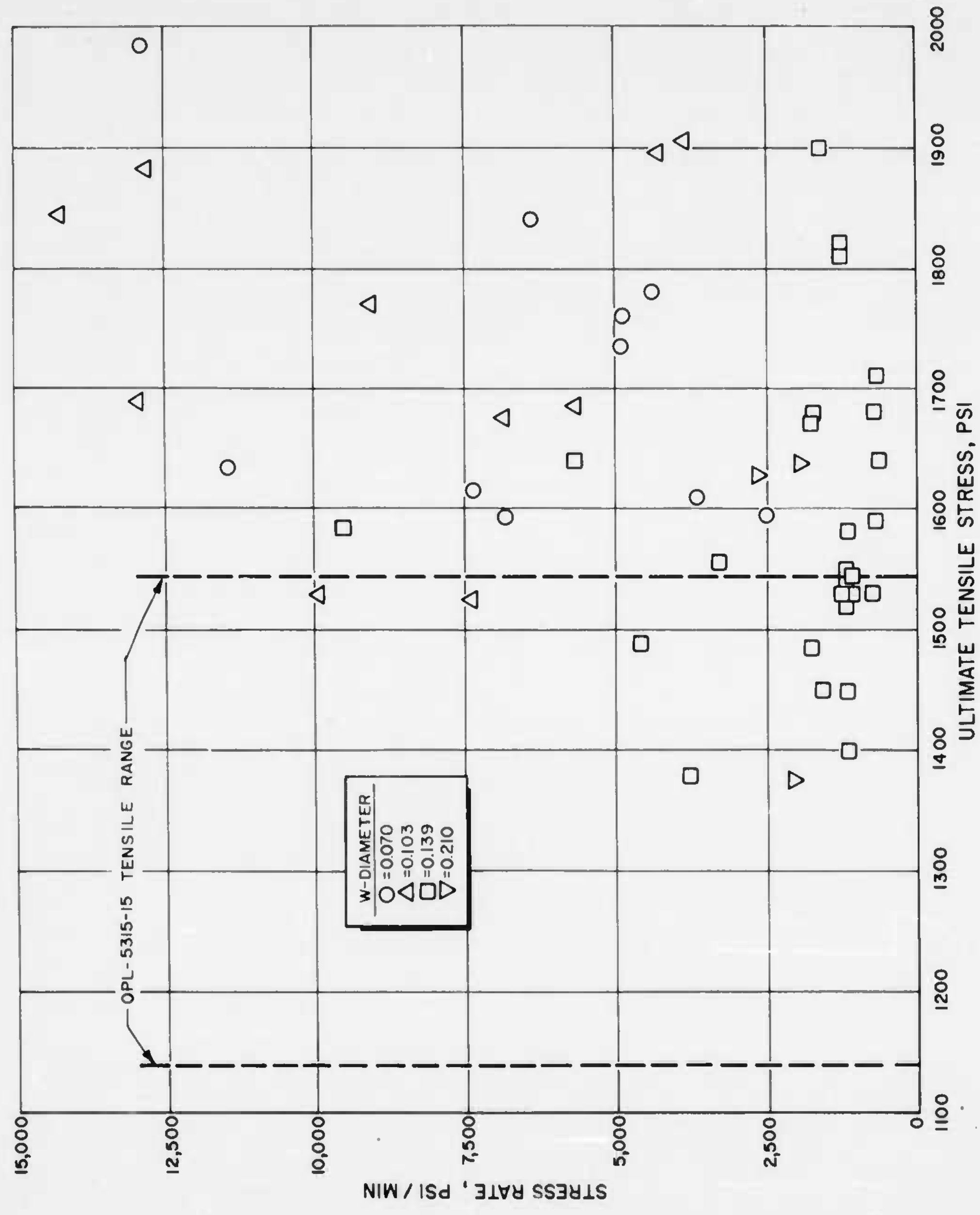
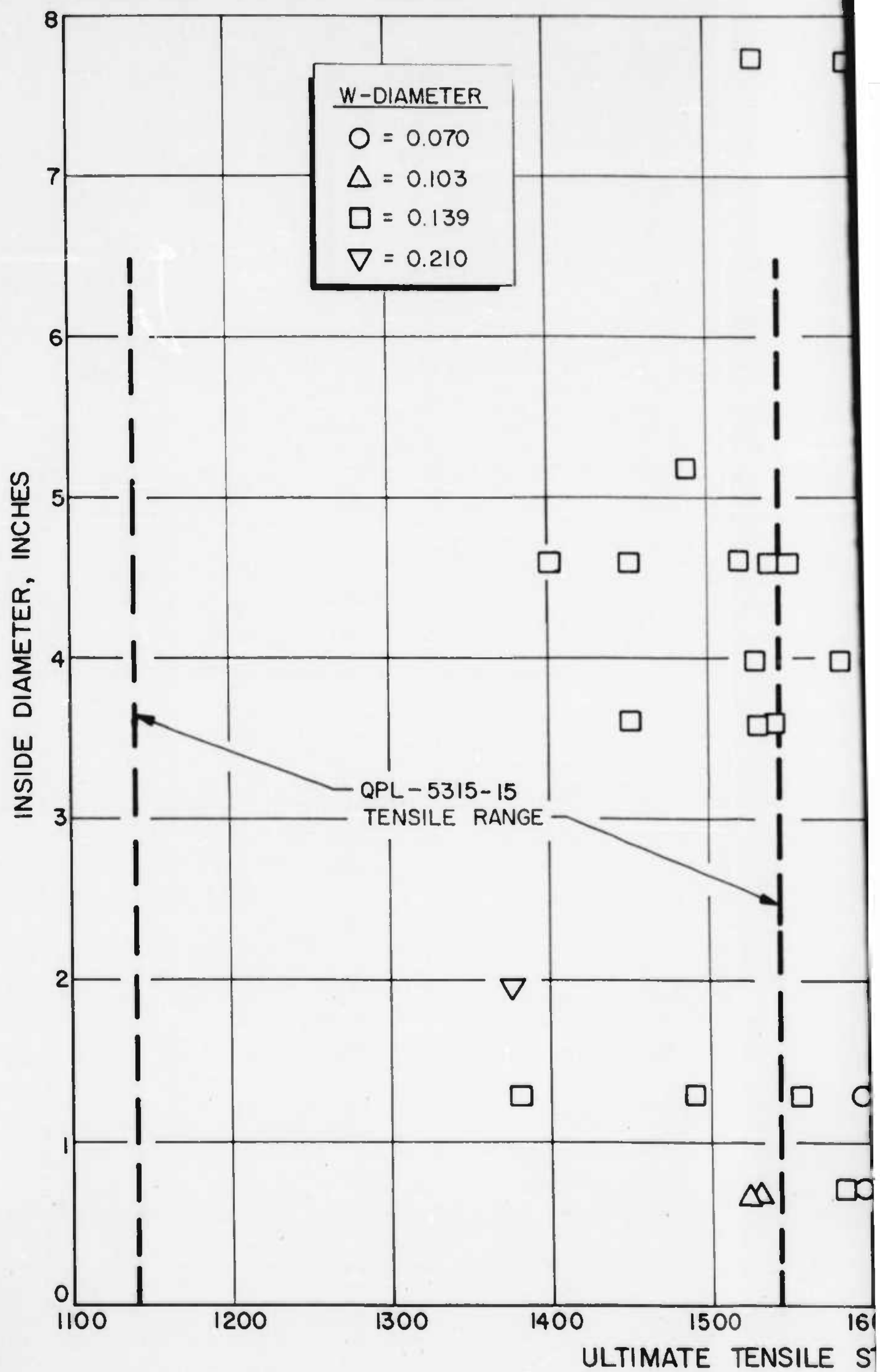


Figure G-2. Stress Rate vs Ultimate Tensile Strength of MS29513 O-Rings With Various Inside and W-Diameters



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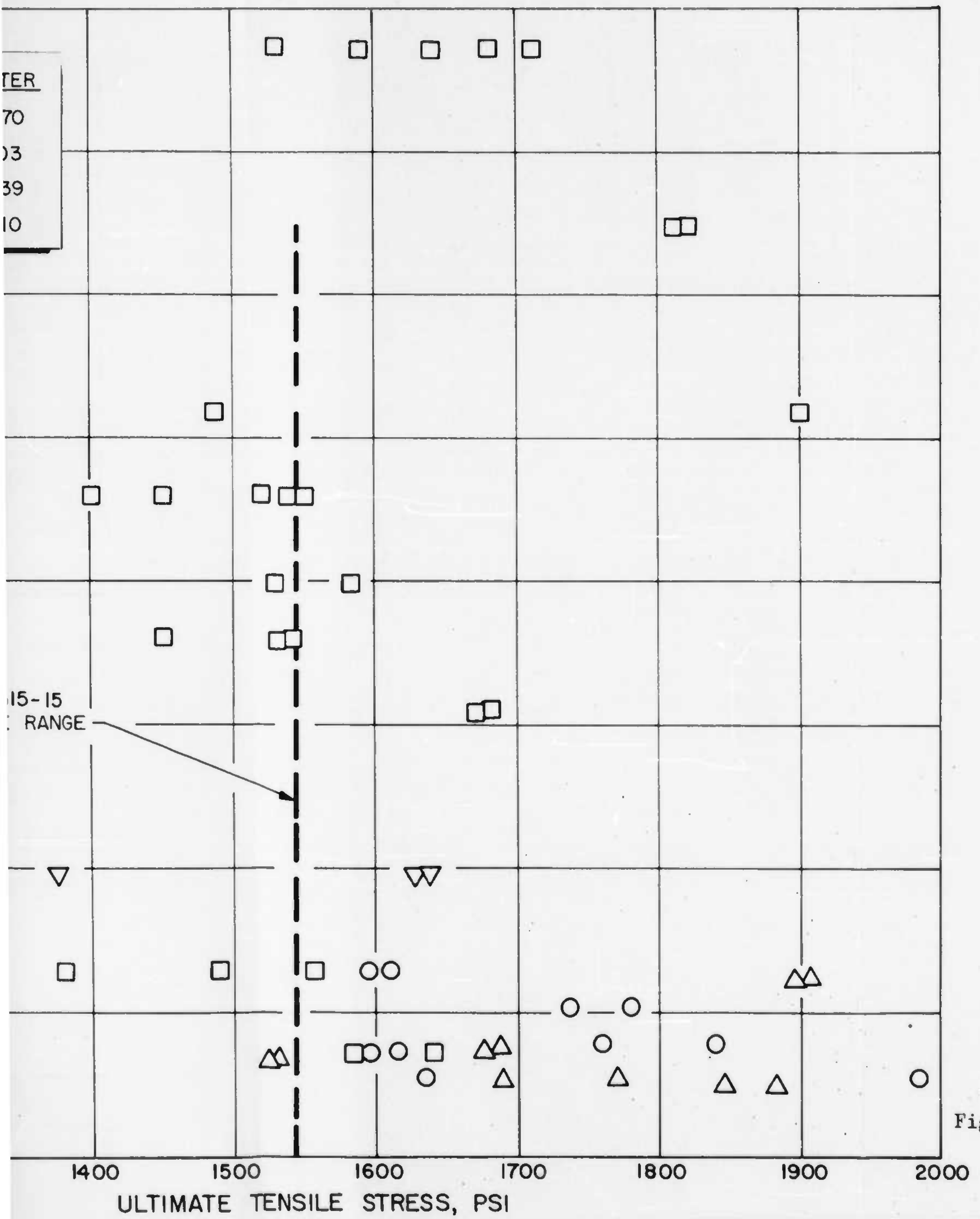


Figure G-3. Inside Diameter vs Ultimate Tensile Strength of MS29513 O-Rings With Various W-Diameters

2

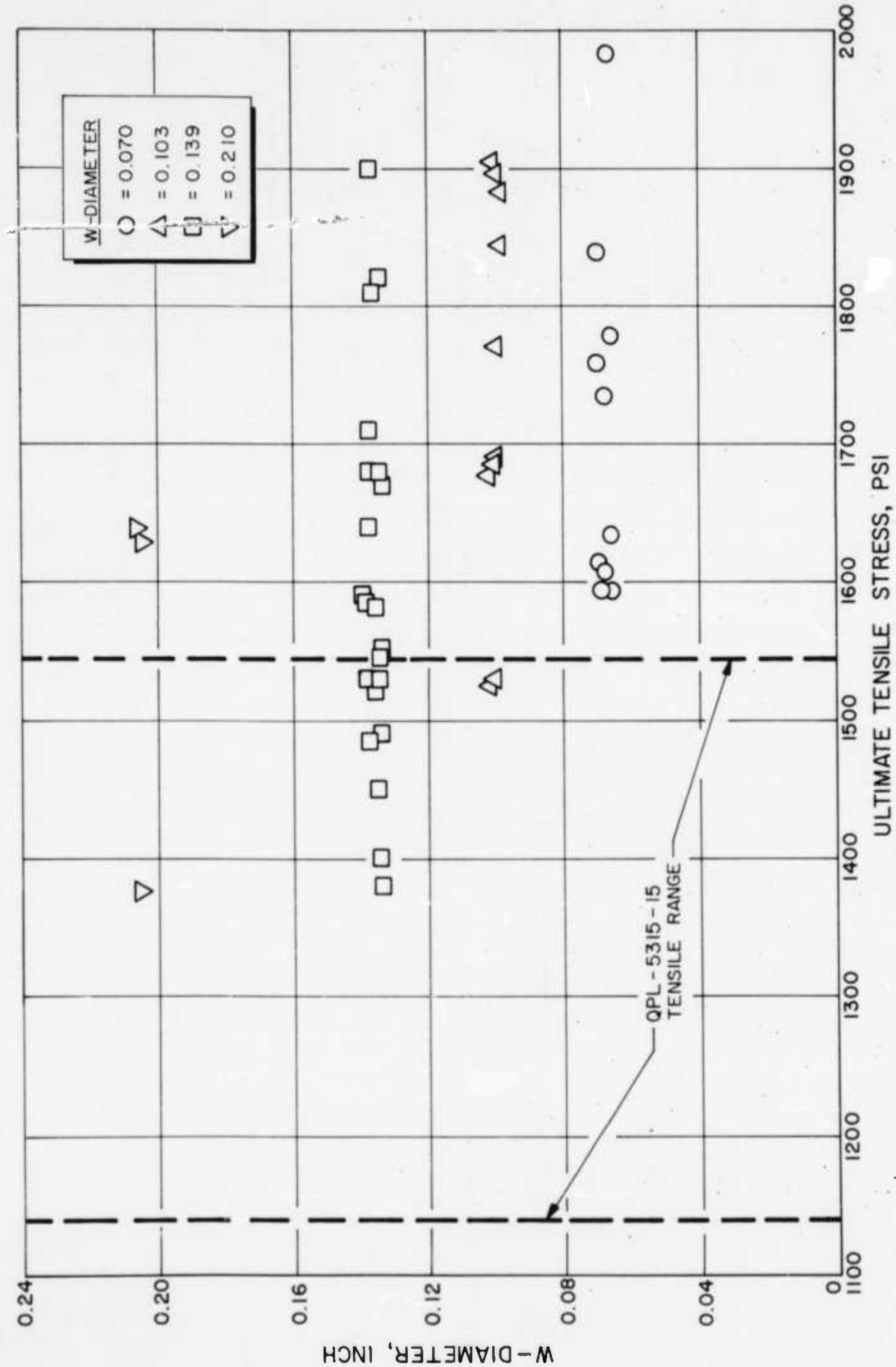


Figure G-4 . W-Diameter vs Ultimate Tensile Strength of MS29513 O-Rings With Various Inside Diameters

TABLE G-2

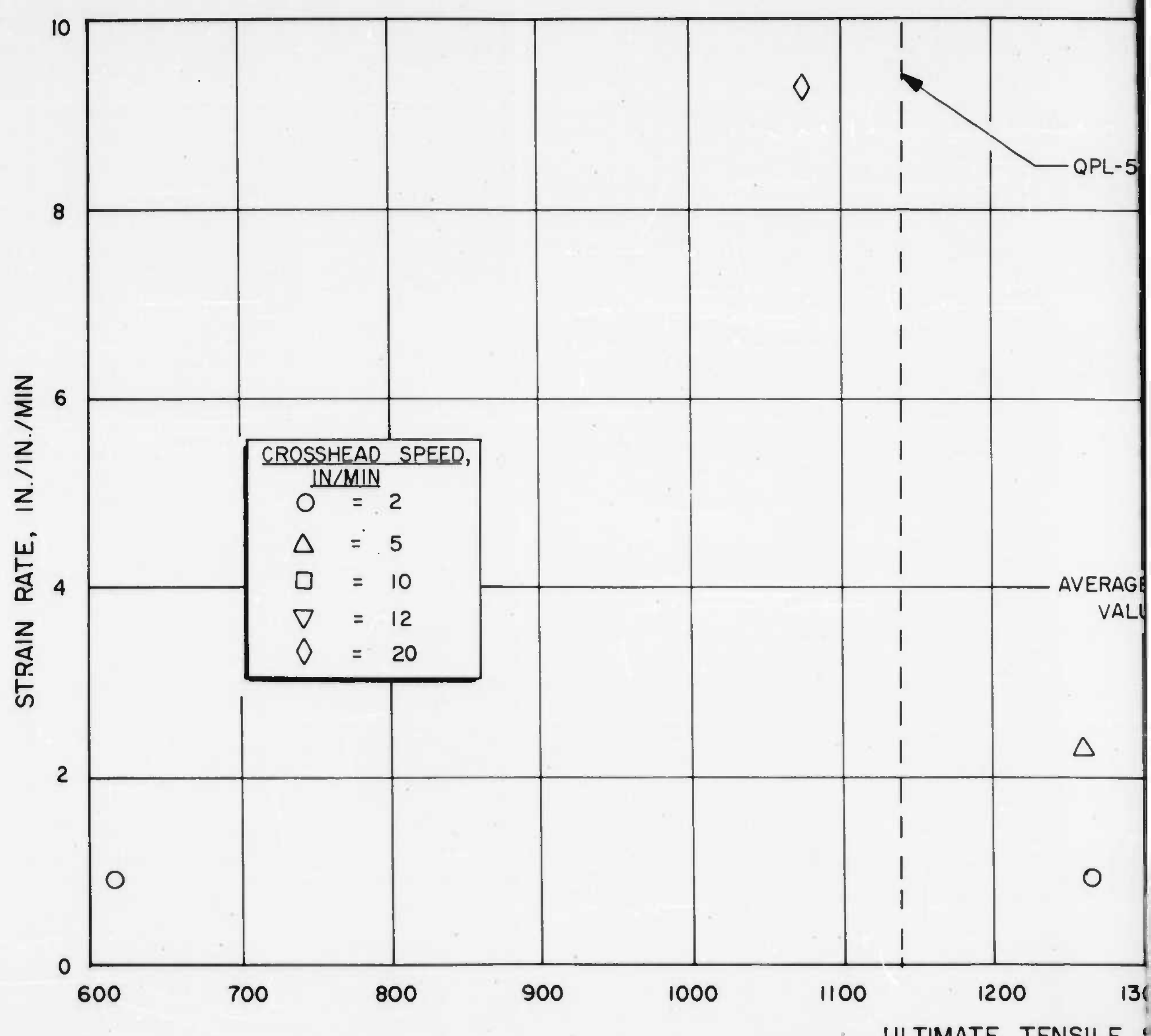
MS29513-218 O-RING DATA

(Varying Crosshead Speeds)

Crosshead Speed, in./min	Specimen Number	Ultimate Tensile Stress, psi	Time to 100% Elongation, minute	Strain Rate, in./in.-min	Tensile Stress at 100% Elongation, psi	Stress Rate, psi/min	Ultimate Elongation, %
2	1	1535	1.08	0.925	386	357	257
	2	1790			522	484	280
	3	1740			466	432	295
	4	1600			454	420	254
	5	1635			480	444	260
	6	1400			450	416	220
	7	1575			432	400	260
	8	1265			496	460	185
	9	1725			450	416	283
	10	1885			435	403	314
5	A-1	1770	0.431	2.32	473	1100	275
	A-2	1950			585	1360	278
	A-3	1810			568	1320	280
	A-4	1795			431	1000	310
	A-5	1770			458	1062	281
	A-6	1840			432	1000	320
	A-7	1880			485	1125	303
	A-8	1820			461	1070	300
	A-9	1725			414	960	273
	A-10	1260			550	1278	175
10	B-1	1750	0.216	4.63	455	2105	275
	B-2	1770			514	2380	294
	B-3	1870			—	—	290
	B-4	1635			479	2220	263
	B-5	1800			430	1990	294
	B-6	1555			495	2290	254
	B-7	1840			507	2350	303
	B-8	1910			420	1945	310
	B-9	1860			[illegible]	[illegible]	[illegible]

	A-6	1840			432	1000	320
	A-7	1880			485	1125	303
	A-8	1820			461	1070	300
	A-9	1725			414	960	273
	A-10	1260			550	1278	175
10	B-1	1750	0.216	4.63	455	2105	275
	B-2	1770			514	2380	294
	B-3	1870			—	—	290
	B-4	1635			479	2220	263
	B-5	1800			430	1990	294
	B-6	1555			495	2290	254
	B-7	1840			507	2350	303
	B-8	1910			420	1945	310
	B-9	1860			443	2050	310
	B-10	1820			490	2270	284
12	C-1	1870	0.18	5.55	425	2360	303
	C-2	—			—	—	267
	C-3	1660			490	2720	250
	C-4	1720			490	2720	265
	C-5	1835			503	2795	298
	C-6	1800			463	2575	295
	C-7	1875			450	2500	294
	C-8	1890			425	2360	298
	C-9	1350			480	2670	212
	C-10	1790			438	2435	308
20	D-1	1690	0.108	9.25	480	4450	240
	D-2	1890			433	4010	313
	D-3	1075			433	4010	182
	D-4	1520			496	4600	232
	D-5	1675			496	4600	261
	D-6	1680			461	4270	268
	D-7	1710			433	4010	250
	D-8	1775			468	4330	273
	D-9	1935			425	3940	296
	D-10	1835			450	4170	278

2


QPL-5
AVERAGE
VALU
CROSSHEAD SPEED, IN/MIN
○ = 2
△ = 5
□ = 10
▽ = 12
◇ = 20
STRAIN RATE, IN./IN./MIN
10
8
6
4
2
0
600
700
800
900
1000
1100
1200
130
ULTIMATE TENSILE

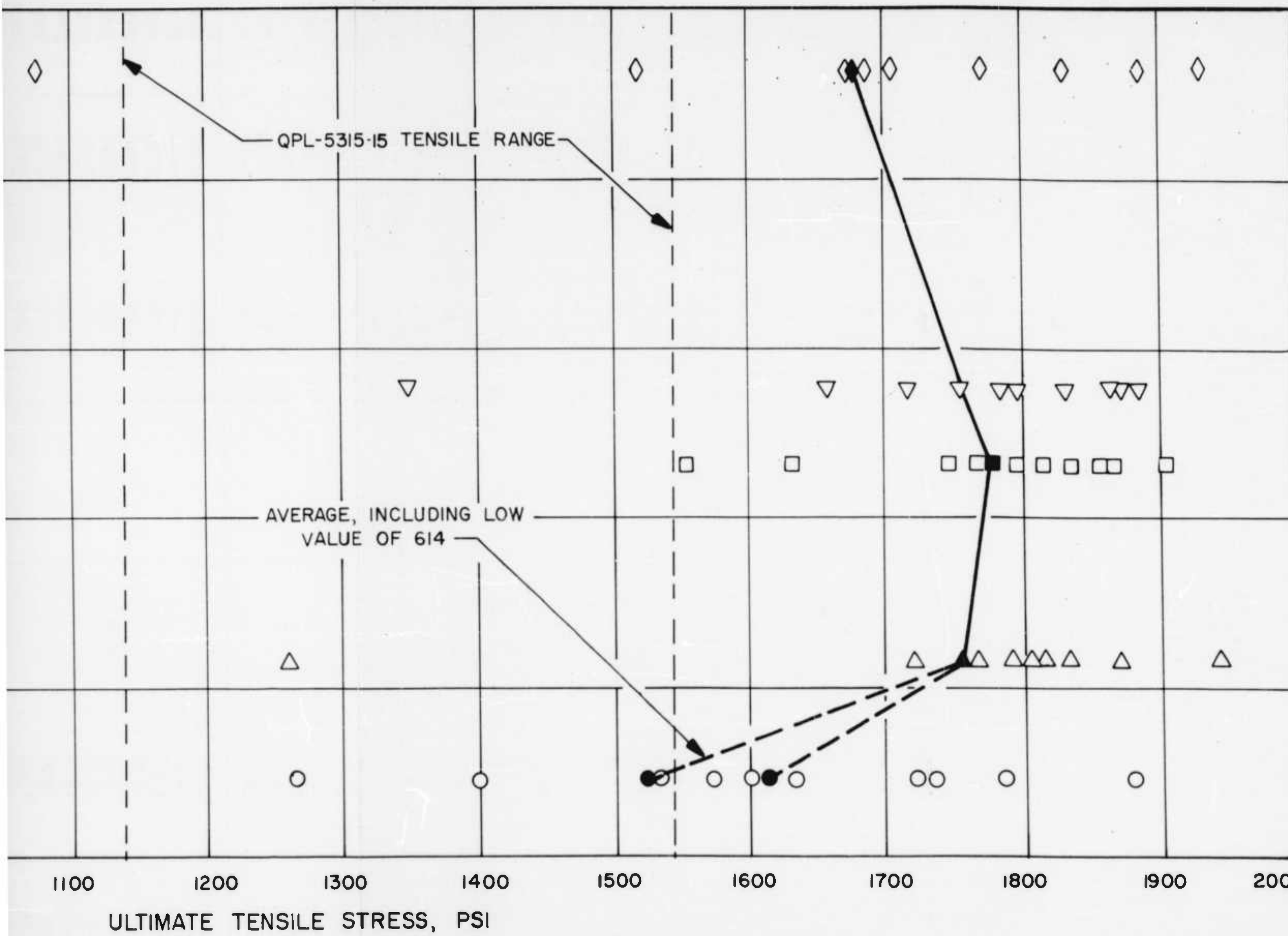
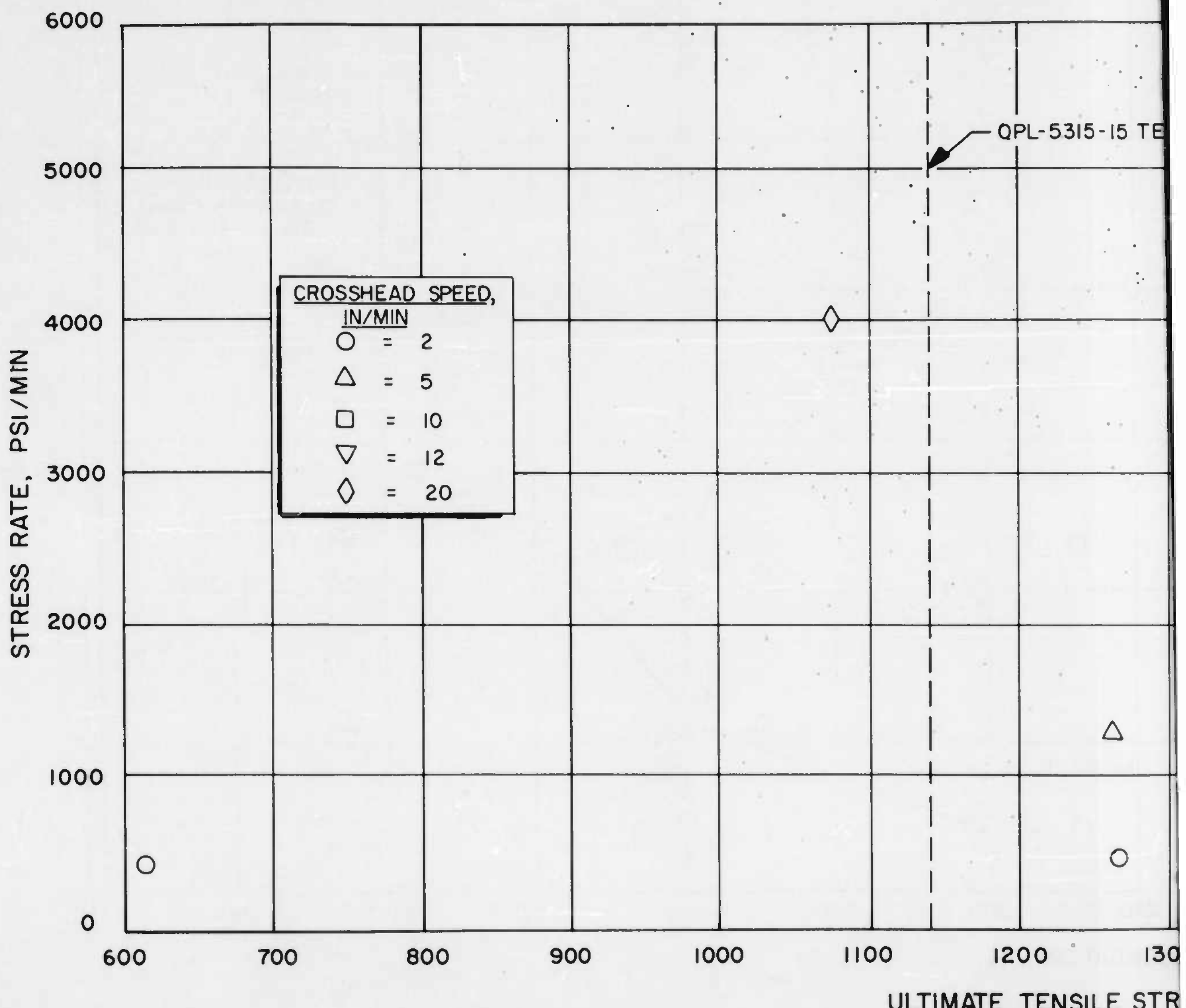


Figure G-5. Strain Rate vs Ultimate Tensile Strength of MS29513-218 O-Rings at Varying Crosshead Speeds

2



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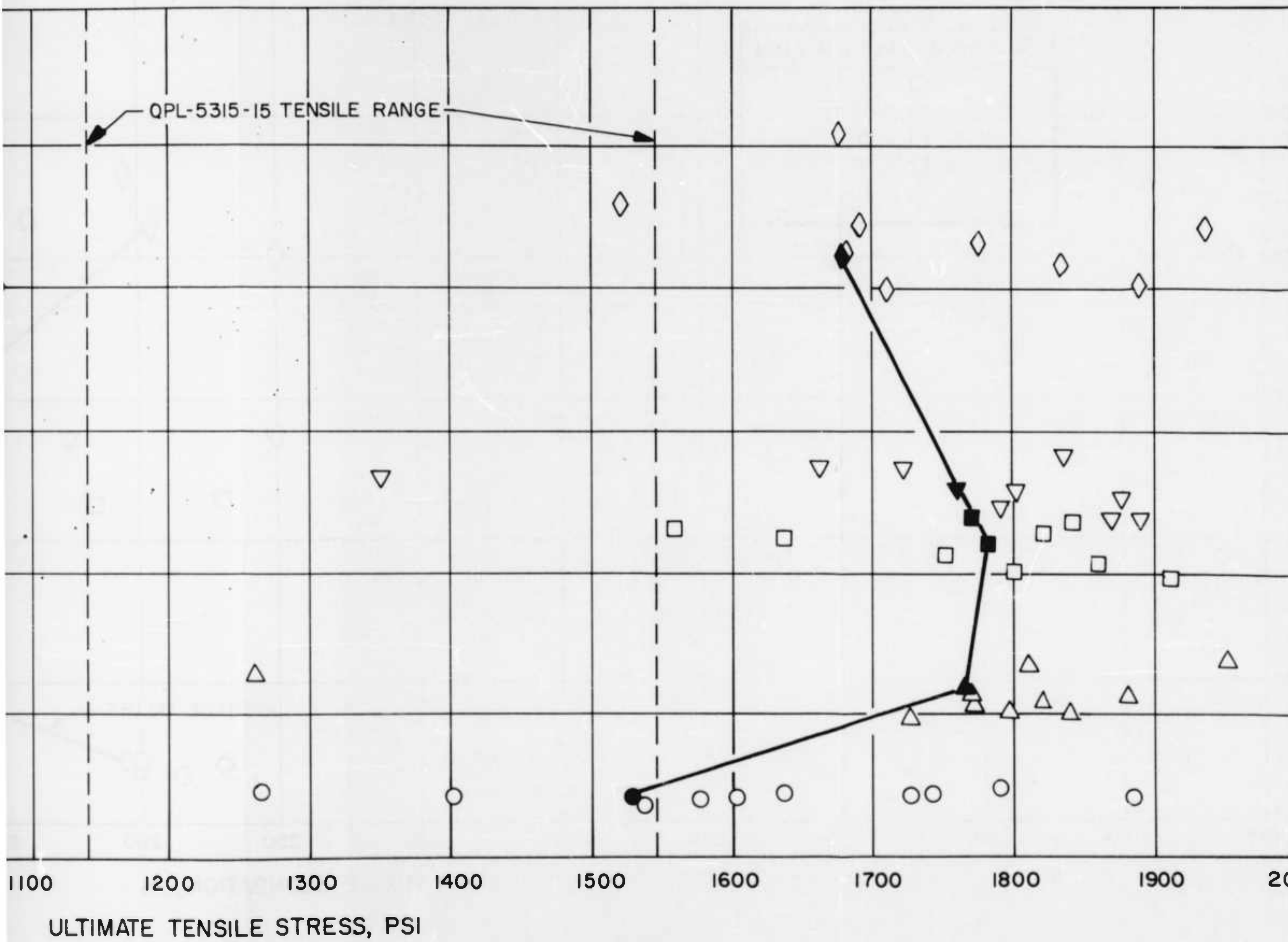

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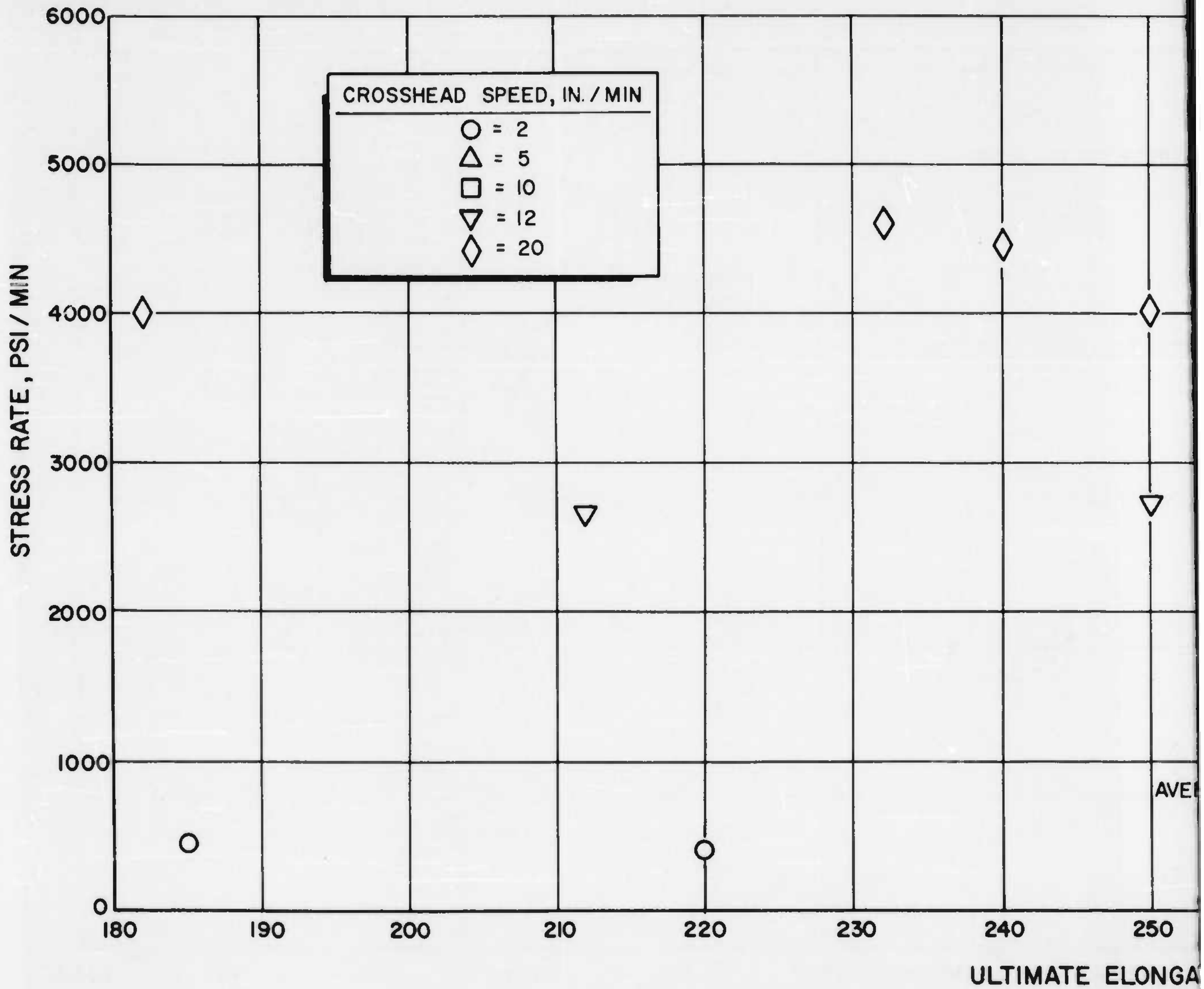
Figure G-6. Stress Rate vs Ultimate Tensile Strength of MS29513-218 O-Rings at Varying Crosshead Speeds



CROSSHEAD SPEED, IN. / MIN
○ = 2
△ = 5
□ = 10
▽ = 12
◇ = 20
STRESS RATE, PSI / MIN
6000
5000
4000
3000
2000
1000
0
180
190
200
210
220
230
240
250
ULTIMATE ELONGA
AVE

1

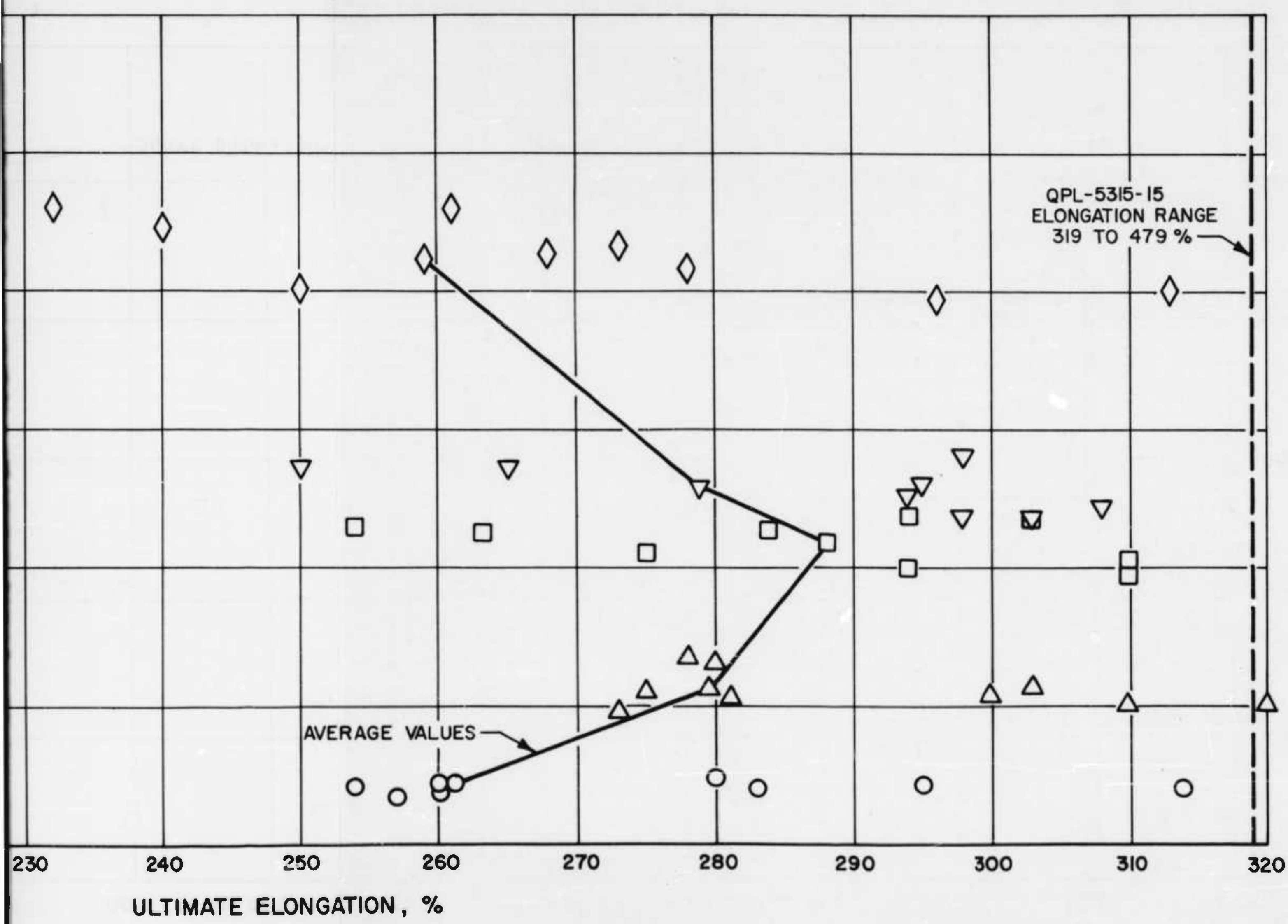


Figure G-7. Stress Rate vs Ultimate Elongation of MS29513-218 O-Rings at Varying Crosshead Speeds

2

TABLE G-3

MS29513-325 O-RING DATA

(Varying Crosshead Speeds)

Specimen Number	Crosshead Speed, in./min	Ultimate Tensile Stress, psi	Time to 100% Elongation, minute	Strain Rate, in./in.-min	Tensile Stress at 100% Elongation, psi	Stress Rate, psi/min	Ultimate Elongation, %
A-1	2	1370	1.322	0.755	522	394	225
A-2		1180			543	411	190
A-3		1360			554	419	210
A-4		1200			700	529	170
A-5		1300			700	529	170
A-6		1255			765	579	168
A-7		1260			764	578	165
A-8		1185			718	543	165
A-9		1230			748	566	164
A-10		1245			590	446	200
B-1	5	1330	0.529	1.89	734	1390	178
B-2		1200			703	1330	160
B-3		1330			734	1388	180
B-4		1195			740	1400	220
B-5		1535			463	875	250
B-6		1245			715	1353	170
B-7		1228			671	1270	195
B-8		1200			746	1412	165
B-9		1270			850	1608	160
B-10		1430			745	1410	186
C-1	10	1530	0.2645	3.78	473	1788	260
C-2		1470			567	2143	255
C-3		1250			569	2150	220
C-4		1410			577	2182	154
C-5		1230			643	2430	200
C-6		1350			655	2475	200
C-7		1420			532	2010	242
C-8		1450			494	1865	260
C-9		1400			860	3250	195
C-10		1390			644	2430	228

B-7		1228			671	1270	195
B-8		1200			746	1412	165
B-9		1270			850	1608	160
B-10		1430			745	1410	186
C-1		1530			473	1788	260
C-2		1470			567	2143	255
C-3		1250			569	2150	220
C-4		1418			573	3183	154
C-5	10	1270	0.2045	3.70	643	2430	200
C-6		1350			655	2475	200
C-7		1420			532	2010	242
C-8		1450			494	1865	260
C-9		1400			860	3250	195
C-10		1390			644	2430	228
D-1		1480			557	2530	260
D-2		1375			872	3960	180
D-3		1440			932	4230	180
D-4		1365			743	3370	180
D-5	12	1370	0.2203	4.54	552	2502	230
D-6		1350			839	3810	178
D-7		1400			644	2920	206
D-8		1520			773	3510	205
D-9		1440			568	2580	295
D-10		1470			460	2085	240
E-1		1420			833	6300	180
E-2		1480			554	4190	230
E-3		1350			468	3540	230
E-4		1340			943	7130	160
E-5	20	1465	0.1322	7.55	763	5770	202
E-6		1450			868	6560	170
E-7		1490			582	4400	225
E-8		1435			552	4170	224
E-9		1490			863	6530	180
E-10		1430			692	5240	170

2

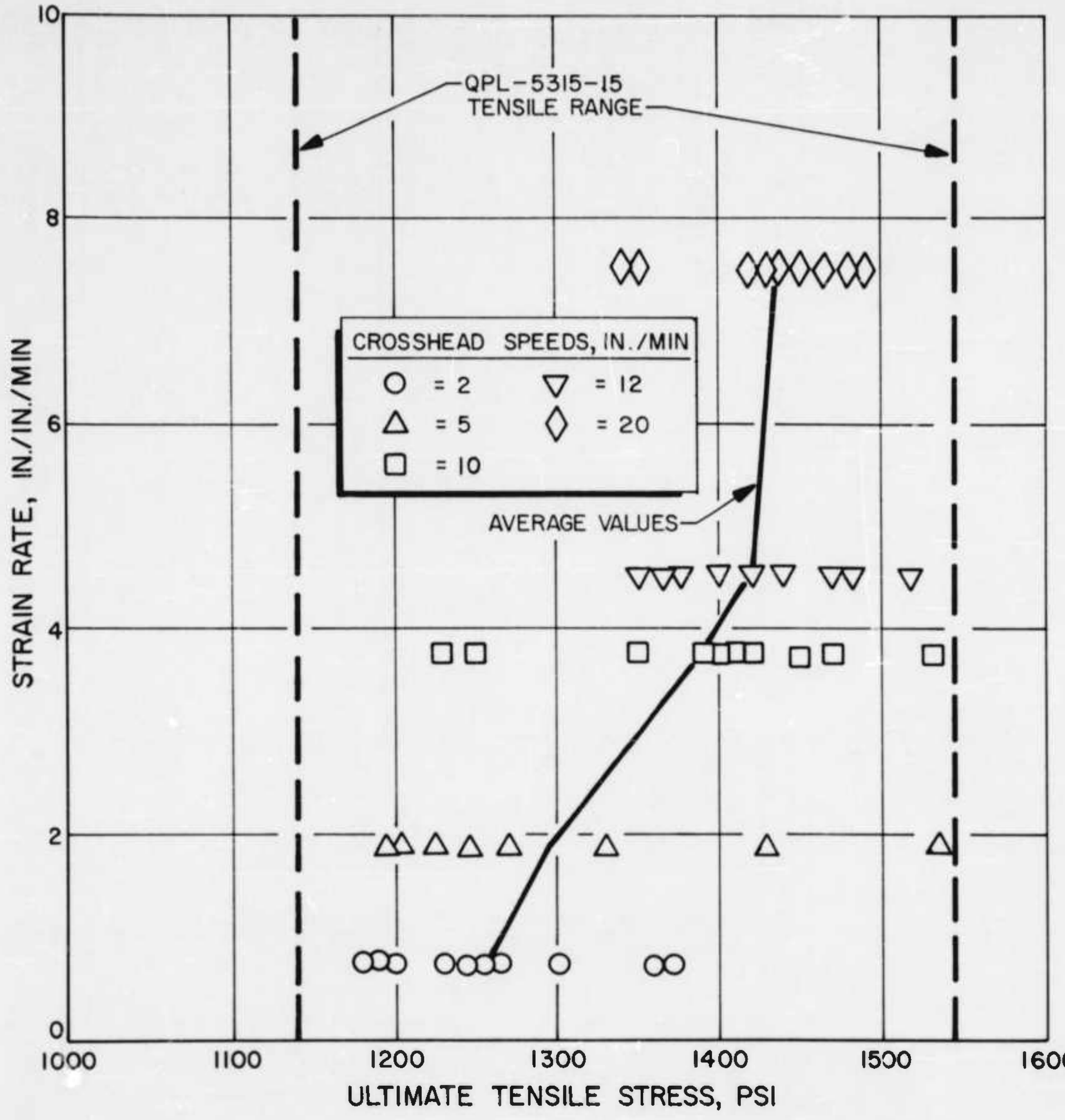


Figure G-8 . Strain Rate vs Ultimate Tensile Strength of MS29513-325 0-Rings at Varying Crosshead Speeds

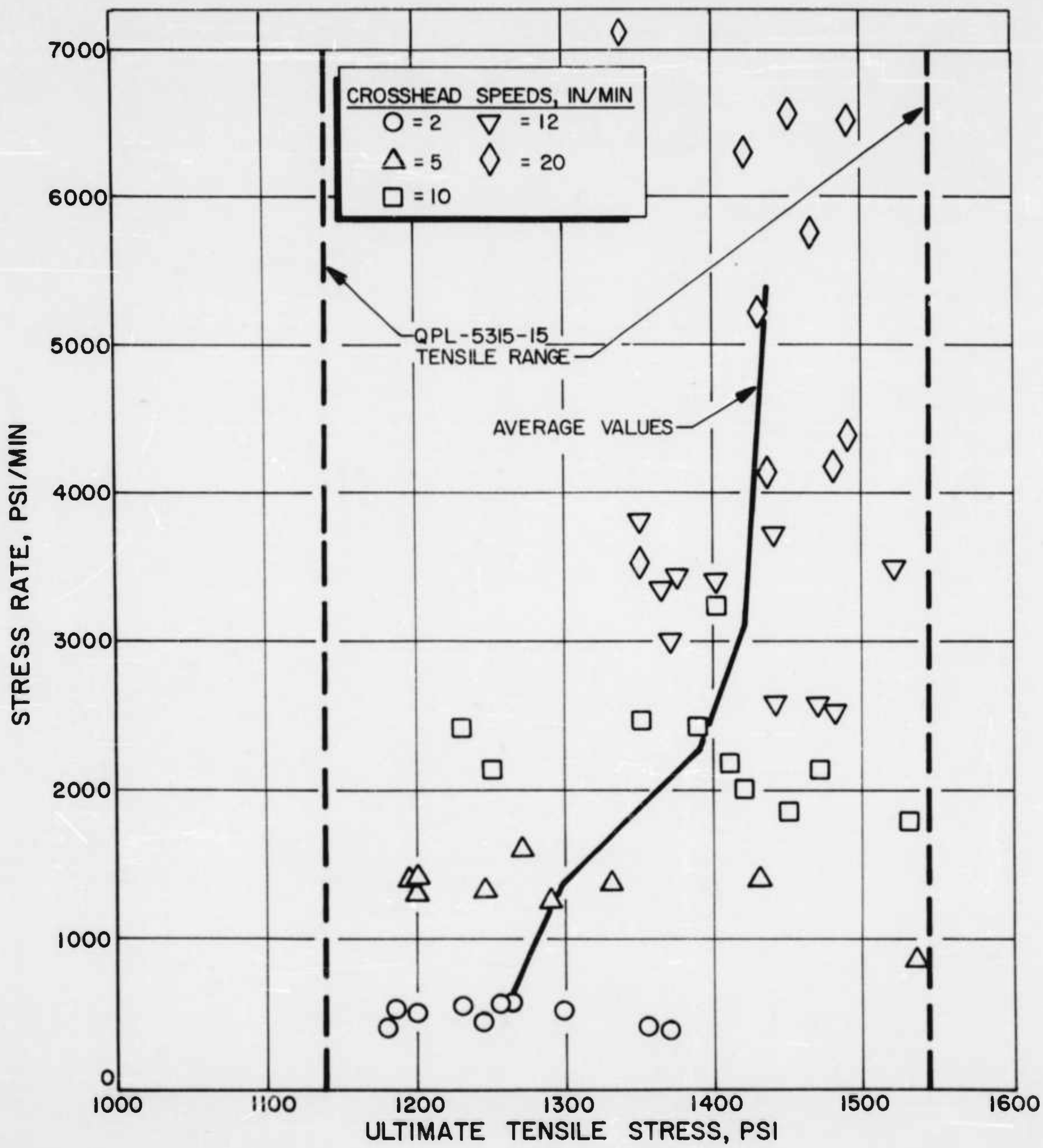
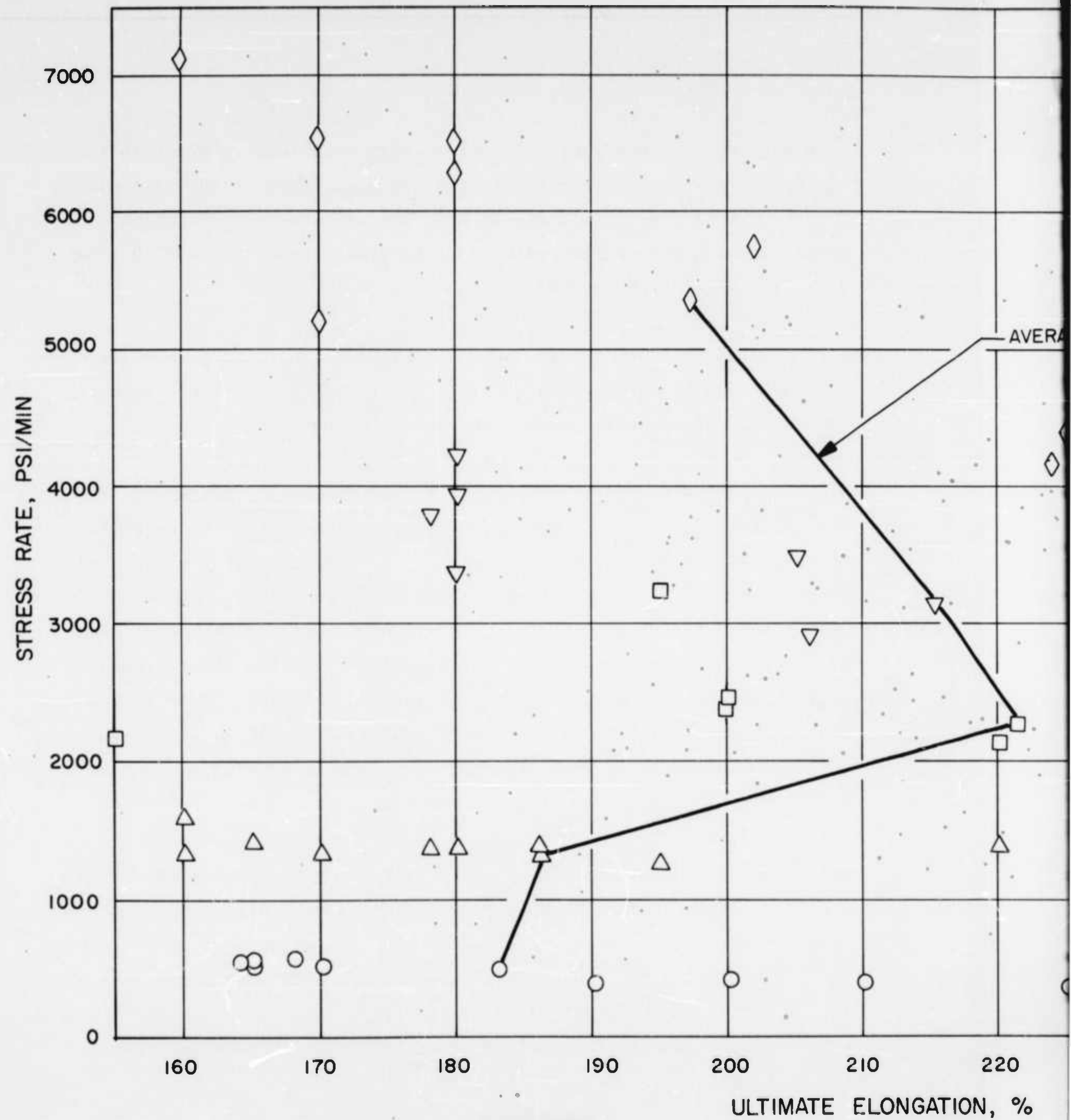


Figure G-9. Stress Rate vs Ultimate Tensile Strength of MS29513-325 O-Rings at Varying Crosshead Speeds



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R-5253

FORM R 18-G-18

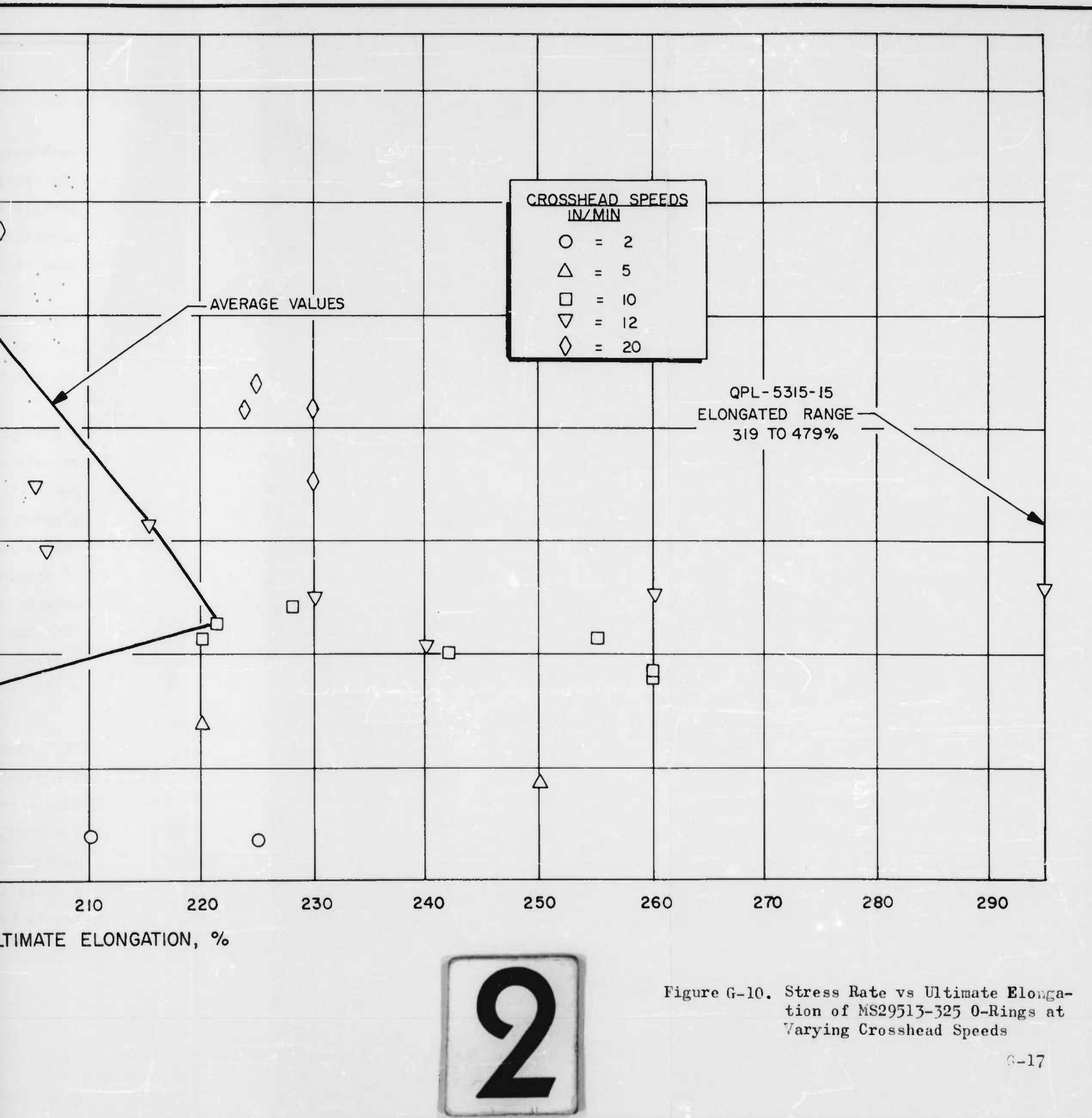

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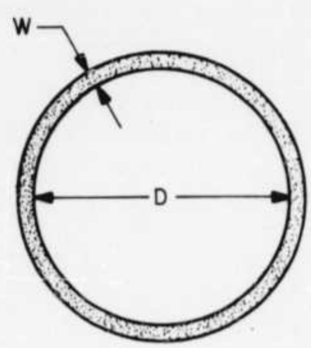
Figure G-10. Stress Rate vs Ultimate Elongation of MS29513-325 O-Rings at Varying Crosshead Speeds much more scatter and generally, were, higher in tensile strength than the specified range. This scattering and high level of the ultimate tensile stress indicates that, to meet the military specification, the manufacturer might exert greater care in producing MS29513-325 O-rings than is taken in the production of other size O-rings.

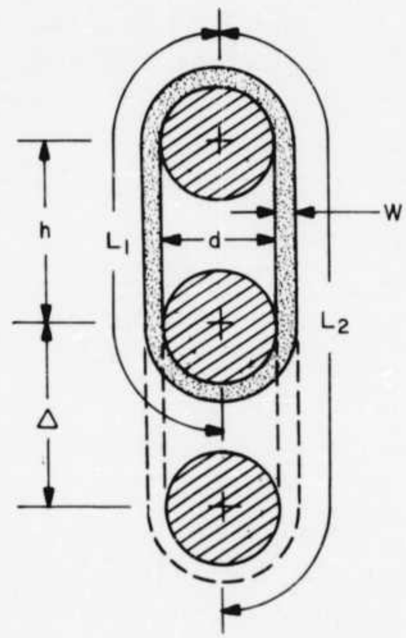
All MS29513 sizes other than the -325 size are qualified by results of the -325 tensile tests, consequently, quality control efforts probably are not as stringent for sizes other than the -325 size.

Figure G-8 shows that, for the vendor in question, -325 rings will give results that fall well within the QPL-5315-15 limits over an eight-fold range of strain rates. Similar results are obtained for the same data plotted on a function of stress rate to 100% elongation. The data for -218 size rings (Fig.G-5 and G-6) tested over virtually the same range of strain and stress rates show that virtually all of the averages fall outside the specification limits. While it is not possible to state that the tested -218 rings are outside the specification, it is equally difficult to attribute such differences to simply running 0.210- and 0.139-inch W- diameter O-rings by the same test method.

This study was made possible by the inclusion (in the fifteenth issue of QPL-5315) of the physical property qualification values for all of the manufacturers qualified under MIL-P-5315A, the procurement specification for MS29512 and MS29513 O-rings. These data, which were previously almost unobtainable, are of great value in studies of this type and are virtually a necessity if meaningful studies of age deterioration and service life are to be made.

STRAIN RATE DERIVATION





Assumptions

1. Stretch throughout length of O-ring is uniform due to rotating mandrels.
2. No tensile stress is introduced into O-ring when changing to oval shape on mandrels.
3. The cross-sectional area of the O-ring does not change during testing.

Unit Strain

$$\delta = \frac{L_2 - L_1}{L_1}$$

$$\delta = \frac{[h + \pi/2\,(d + w) + \Delta] - [h + \pi/2\,(d + w)]}{[h + \pi/2\,(d + w)]}$$

$$\delta = \frac{\Delta}{h + \pi/2\,(d + w)}$$

Initial Distance Between Mandrels

$$h = \frac{1}{2}[\pi\,(D + w) - \pi\,(d + w)]$$

$$h = \frac{1}{2}[\pi\,(D - d)$$

Time For Crosshead Travel To Failure

$$t = \frac{\text{ultimate elongation of O-ring}}{\text{crosshead speed}}$$

$$t = \frac{\Delta}{S}$$

Strain Rate

$$\delta_r = \frac{\delta}{t}$$

$$\delta_r = \frac{\dfrac{\Delta}{h + \pi/2\,(d + w)}}{\dfrac{\Delta}{S}}$$

$$\delta_r = \frac{S}{\frac{1}{2}\left[\pi \left(D-d \right) \right] + \frac{\pi}{2}\left(d + w \right)}$$

$$\delta_r = \pi \frac{2S}{\left(D + w \right)}$$